SULPHUR DIOXIDE:

ENVIRONMENTAL EFFECTS,

FATE AND BEHAVIOUR

Alberta
ENVIRONMENT

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Sulphur Dioxide: Environmental Effects, Fate and Behaviour

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FOREWORD

Alberta Environment maintains Ambient Air Quality Objectives[1] to support air quality management in Alberta. Alberta Environment currently has ambient objectives for thirty-four substances and five related parameters. These objectives are periodically updated and new objectives are developed as required.

With the assistance of the Clean Air Strategic Alliance, a multi-stakeholder workshop was held in October 2000 to set Alberta's priorities for the next three years. Based on those recommendations and the internally identified priority items by Alberta Environment, a three-year work plan ending March 31, 2004 was developed to review four existing objectives, create three new objectives for three families of substances, and adopt six new objectives from other jurisdictions.

This document is one of a series of documents that presents the scientific assessment of environmental effects, fate and behaviour of sulphur dioxide that will be used for review of the existing objective.

Laura Blair
Project Manager
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[1] **NOTE**: The *Environmental Protection and Enhancement Act*, Part 1, Section 14(1) refers to "ambient environmental quality objectives" and uses the term "guidelines" in Section 14(4) to refer to "procedures, practices and methods for monitoring, analysis and predictive assessment." For consistency with the *Act*, the historical term "ambient air quality guidelines" is being replaced by the term "ambient air quality objectives." This document was prepared as the change in usage was taking place. Consequently any occurrences of "air quality guideline" in an Alberta context should be read as "air quality objective."

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SUMMARY

Sulphur dioxide (SO_2) is a colourless, non-flammable gas. The most significant anthropogenic emission sources of SO_2 are from combustion of sulphur-containing fossil fuels, smelting sulphide ores, and petroleum refining. Other less significant sources include chemical and allied products manufacturing, metal processing, other industrial processes, and vehicle emissions. Based on data from 1990 to 2000, annual mean SO_2 concentrations in Canadian cities range from approximately 3 $\mu g/m^3$ (1 ppb) in Winnipeg, Regina and Saskatoon to as high as 26 $\mu g/m^3$ (10 ppb) in Halifax. Annual mean SO_2 concentrations in Edmonton and Calgary were 8 $\mu g/m^3$ (3 ppb).

Once SO_2 is released into the atmosphere, it may be converted to other compounds and/or removed from the atmosphere by various mechanisms. Processes such as oxidation, wet deposition, dry deposition, absorption by vegetation and by soil, dissolution into water and other processes contribute to the removal of SO_2 from the atmosphere.

Acute exposure (single exposures) to SO_2 has produced immediate bronchial constriction, narrowing of the airways, increased pulmonary resistance, and increased airway reactivity at concentrations less than 2.6 mg/m^3 in experimental animals. Acute exposures to experimental animals has also produced changes in metabolism and irritation to the mucus membranes in eyes at 26 mg/m^3.

Unlike acute exposures, chronic exposures do appear to affect pulmonary resistance. For example, chronic exposure to 2.6 mg/m^3 has caused swelling of mucosal tissues and increased secretions producing respiratory damage similar to chronic bronchitis in experimental animals. Increased mucus secretion and decreased ability of the cilia in the respiratory tract results in a reduced ability of the respiratory tract to clear particulates from the airways. Exposure may augment pulmonary allergic reactions, and increase susceptibility to bacterial infections.

There are few studies describing effects of SO_2 only in livestock and/or wildlife. Ambient exposures are commonly associated with smoke/particulate matter and other gases (including sulphuric acid). It is difficult to clearly determine which constituent is producing adverse health effects and what effects may be synergistic. Clinical follow-up of accidental exposure of cattle to sulphur dioxide has indicated that it can produce mild bronchial constriction, changes in metabolism, and irritation of the respiratory tract and eyes. Exposure conditions (ambient levels and durations) that produced these effects were not known. Study of livestock (cattle, hogs, and chickens) exposed to SO_2 from gas plants did not demonstrate adverse effects in animal health or productivity.

Air pollution has been attributed to the reduction and impairment of wildlife population, birds, mammals and insects. However, it is difficult to determine whether the effects reported are due to exposures to SO_2, other pollutants, or a combination of exposure to SO_2 and the other pollutants. Adverse effects in wildlife populations may not be a direct response to SO_2 exposure; rather they may be indirectly caused through effects of air pollution on the animal's ecosystem. Materials used for construction of buildings, bridges, etc. are subject to weathering in the form of deterioration or corrosion of the material surfaces under action of meteorological factors (atmospheric carbon dioxide, precipitation, wind, and solar radiation). The presence of air

pollutants – including acid aerosols and their precursors such as SO_2 – can damage or accelerate the aging of material surfaces. With respect to stonework, research indicates that most of the deterioration (erosion) – perhaps greater than 70% – occurs as a result of solubility of the carbonate stone in rain that is in equilibrium with atmospheric carbon dioxide (i.e. as a result of the exposure to clean rain).

Corrosion of metals in the atmosphere is caused by an electrochemical process. SO_2 merely modifies and accelerates corrosion reactions that occur naturally when sufficient moisture is present on a metal surface. Corrosion rates for carbon steel and zinc have been reported in the range of 11 to 13, and 0.5 to 0.5 μm per year, respectively at rural sites in Sweden and Czechoslovakia at SO_2 levels less than 10 $\mu g/m^3$. Corrosion rates reported for aluminum are even lower than that for zinc under comparable SO_2 levels. Pre-1980 studies have indicated corrosion rates for copper in the range 1 to 2.5 μm per year in industrial/urban environments and up to 0.6 μm per year in rural environments from SO_2 exposure. However, caution is warranted about estimating corrosion rates for present conditions from these data because SO_2 levels have decreased since the late 1970s such that the rates at which corrosion to copper occur would be less today.

The most important factors in the deterioration of paint on exterior surfaces are ultraviolet light and atmospheric oxidants, including oxygen and wetness. Reliable data on air pollutant exposure-paint response relationships are limited. However, air pollutants – including SO_2 – are generally recognized to reduce the life of paint, as repainting intervals for exterior surfaces are shorter in more-polluted urban/industrial environments compared to rural environments.

1.0 INTRODUCTION

Alberta Environment establishes Ambient Air Quality Guidelines under Section 14 of the Environmental Protection and Enhancement Act (EPEA). These guidelines are part of the Alberta air quality management system (AENV, 2000). An Ambient Air Quality Guidelines Priority Setting Workshop was held in October 2000 to receive stakeholder input into the priority of substances nominated to the guideline development process. Stakeholders identified the current Alberta Environment sulphur dioxide ambient guideline a priority for review.

1.1 Objective

The main objective of this report is to provide a review of scientific and technical information on sulphur dioxide related to the following areas:

Physical and chemical properties.

Health effects of sulphur dioxide on animals (livestock and wildlife).

Effects of sulphur dioxide on materials (buildings, bridges, statuary, etc.).

Currently used monitoring techniques.

2.0 GENERAL SUBSTANCE INFORMATION

Table 1 provides a list of common synonyms and a list of important identification numbers for sulphur dioxide (SO_2).

Table 1 Identification of Sulphur Dioxide[a]

Property	Value
Formula	SO_2
Structure	O = S = O
CAS Registry number	7446-09-5
RTECS number	WS4550000
UN Number	UN 1079
Common Synonyms	Caswell Number 813 EPA Pesticide 077601 Fermenticide liquid[b] Sulfur dioxide Sulfur superoxide[b] Sulfur oxide Sulfurous acid anhydride Sulfurous anhydride Sulfurous oxide

[a] all data from HSDB, 2002 unless otherwise stated; [b] RSC, 1999.

The two most important uses of sulphur dioxide are as a captive intermediate in the production of sulphuric acid and in the pulp and paper industry (ATSDR, 1998; Weil and Sandler, 1997; IARC, 1992). In the food industry, sulphur dioxide is used as a food preservation agent for fruits, vegetables and cooked meats, as a disinfectant in breweries and food factories, as a fumigant and as a bleaching agent for textiles, straw, gelatine, glue and sugar beet (Genium, 1999; RSC, 1999; ATSDR, 1998; Budavari, 1996). In the petroleum industry, sulphur dioxide is used as catalyst or co-catalyst and as a solvent (ATSDR, 1998; IARC, 1992). Sulphur dioxide is also used as a flotation depressant in the processing of sulphide ores (ATSDR, 1998; IARC, 1992) and is used to reduce residual chlorine in water, wastewater and industrial wastewater treatment systems (Weil and Sandler, 1997; IARC, 1992).

2.1 Physical and Chemical Properties

The physical and chemical properties of sulphur dioxide are summarized in Table 2. SO_2 is a colourless, non-flammable gas (Budavari, 1996). Its odour has been described as sharp (Genium, 1999), pungent (Genium, 1999; Weil and Sandler, 1997; WHO, 1979), choking (Weil and Sandler, 1997), strong (Budavari, 1996), suffocating (Budavari, 1996) and irritating (WHO, 1979). SO_2 dissolves in water to form a slightly acidic aqueous solution (Genium, 1999). The acidic solution is believed to be due to the formation and the subsequent ionization of H_2SO_3 (Weil and Sandler, 1997; Budavari, 1996), however H_2SO_3 in its pure form has not yet been isolated (Weil and Sandler, 1997).

Table 2 Properties of Sulphur Dioxide

Property	Value	Reference
Molecular weight	64.065	Lide, 2002
Physical state	Colourless gas	Lide, 2002
Melting point	-75.5 °C	Lide, 2002
Boiling point	-10.05 °C	Lide, 2002
Specific gravity (liquid)	1.50	RSC, 1999
Specific gravity (gas) (air =1)	2.26 (at 0°C)	Genium, 1999; RSC, 1999
Vapour pressure	338 kPa (at 21°C)	RSC, 1999
	230 kPa (at 10°C)	Weil and Sandler, 1997
	330 kPa (at 20°C)	
	462 kPa (at 30°C)	
	630 kPa (at 40°C)	
Solubility in water	17.7% (at 0°C)	Genium, 1999
	85 g/L (at 25°C)	RSC, 1999
	22.971 g/100 g H_2O (at 0°C)	Weil and Sandler, 1997
	16.413 g/100 g H_2O (at 10°C)	
	11.577 g/100 g H_2O (at 20°C)	
	8.247 g/100 g H_2O (at 30°C)	
	5.881 g/100 g H_2O (at 40°C)	
Solubility	soluble in ethanol, ether and chloroform	Lide, 2002
	moderately soluble in benzene, acetone and carbon tetrachloride	Genium, 1999
	soluble in chloroform, ether, alcohol, methanol	Budavari, 1996
Acid/Base properties	dissolves in water to form a slightly acidic aqueous solution of H_2SO_3	Genium, 1999; Weil and Sandler, 1997
Henry's Law constant	1.42 $mol.L^{-1} atm^{-1}$ (at 25°C)	Berresheim *et al.*, 1995
	1.23 $mol.L^{-1} atm^{-1}$ (at 25°C)	Seinfeld and Pandis, 1998
Octanol water partition coefficient (log K_{ow})	no data	ATSDR, 1998
	-2.20*	Meylan and Howard, 1985, as cited in SRC, 2003
Odour threshold in air	0.1 to 3ppm	Genium, 1999
	0.45 ppm (low)	ATSDR, 1998; Ruth, 1986
	4.8 ppm (high)	
	1.9 ppm (irritating)	
Conversion factors for vapour (at 25 °C and 101.3 kPa)	1 ppm = 2.62 mg/m^3	IARC, 1992

*estimated value

2.2 Emission Sources and Ambient Levels

2.2.1 Natural Sources

Natural sources of sulphur dioxide include volcanoes and volcanic vents, decaying organic matter, solar action on seawater and oxidation of dimethyl sulphide emitted from the ocean (Weil and Sandler, 1997). According to HSDB (2002), although volcanoes are a sporadic source of sulphur dioxide, they are potentially a significant natural source. Decaying organic matter indirectly results in a natural source of SO_2. Decaying organic matter on land, in marshes and in oceans, results in the release of hydrogen sulphide, which is quickly oxidized to SO_2 within hours (HSDB, 2002).

2.2.2 Anthropogenic Sources

2.2.2.1 Global Emissions

On a global scale, anthropogenic emissions represent a significant contribution to the SO_2 emitted to the atmosphere (IARC, 1992) and these emissions are approximately equal to natural emissions (WHO, 1979).). Friend (1973) estimates that, on a global basis, 75 to 85% of SO_2 emissions are the result of fossil fuel combustion, while the remainder of the emissions is the result of refining and smelting. It is estimated that approximately 93% of the global SO_2 emissions are emitted in the northern hemisphere and the remaining 7% are emitted in the southern hemisphere (WHO, 1979). The greatest anthropogenic sources of SO_2 result from the combustion of fossil fuels and from the smelting sulphide ores (Weil and Sandler, 1997). Another significant source is petroleum refining (HSDB, 2002). Other less significant sources include chemical and allied products manufacturing, metal processing, other industrial processes and vehicle emissions (ATSDR, 1998).

2.2.2.2 Emissions in Canada and Alberta

According to Environment Canada (2001a), the industrial sectors responsible for the largest emissions of SO_2 in Canada are the smelting of metal concentrates and power generation. In Alberta, the industrial activities leading to the largest releases of SO_2 are upstream oil and gas activities (which includes natural gas processing), electric power generation and oil sands activities.

Emissions of SO_2 in Canada were estimated at 2633 kilotonnes in 1995 and 2499 kilotonnes in 1999. Of the provinces and territories, Alberta is the second largest emitter of SO_2, with emissions of 608 kilotonnes in 1995 and 548 kilotonnes in 1999. Alberta's SO_2 emissions represented approximately 21% of Canada's total SO_2 emissions. Environment Canada (2001a) predicts that SO_2 emissions in Canada and Alberta will increase to 2793 and 590 kilotonnes, respectively in 2005. The increase in Alberta's emissions is mainly attributed to increases in activities in the upstream oil and gas sector and in the oil sands sector (Environment Canada, 2001a). More detailed emissions data may be found in Environment Canada (2002; 2001a, b).

2.2.3 *Ambient Levels*

In dry, unpolluted atmospheric conditions, it is estimated that the average SO_2 concentration ranges from 0.03 to 0.3 $\mu g/m^3$ (10^{-2} to 10^{-1} parts per billion or ppb) (Harrison, 1990). In remote areas, SO_2 concentrations range 0.13 to 0.31 $\mu g/m^3$ (0.05 to 0.12 ppb) (Weil and Sandler, 1997). In urban and industrialized areas, SO_2 concentrations range from 2.6 to 2600 $\mu g/m^3$ (1 to 1000 ppb) (Weil and Sandler, 1997). A survey by the World Health Organization (WHO) of urban areas showed annual mean SO_2 concentrations ranging from 20 to 60 $\mu g/m^3$ (7 to 21 ppb) and daily means rarely exceeding 125$\mu g/m^3$ (44 ppb) (WHO, 2000). IARC (1992) presents data for ambient air concentrations of SO_2 in different parts of the world. According to Katz (1977), the low ambient SO_2 concentrations in urban areas reflect the ability of certain meteorological factors to disperse SO_2 emitted from strong sources.

More recent data for urban areas in Canada (CASA, 2003a) provides annual mean SO_2 concentrations ranging from approximately 3 $\mu g/m^3$ (1 ppb) in Winnipeg, Regina and Saskatoon to as high as 26 $\mu g/m^3$ (10 ppb) in Halifax. Annual mean SO_2 concentrations in Edmonton and Calgary were 8 $\mu g/m^3$ (3 ppb) (CASA, 2003a). Concentrations of SO_2 in Edmonton and Calgary are lower than in most other Canadian cities. Higher SO_2 concentrations in eastern Canada are attributed to local industry and to the transport of SO_2 from sources in the United States (CASA, 2003b).

Kiely *et al.* (1995) reported annual mean hourly SO_2 levels, measured in Montreal, Toronto, and Vancouver, averaged over a number of sites in each respective city for the five-year period from 1988 to 1992. The range of annual mean hourly SO_2 levels for the respective cities were:

Montreal - 13 to 21 $\mu g/m^3$.

Toronto - 13 to 16 $\mu g/m^3$.

Vancouver - 11 to 12 $\mu g/m^3$.

Annual mean hourly SO_2 levels measured in east Edmonton (adjacent to the Strathcona industrial corridor) during the same five-year period ranged from 5 to 8 $\mu g/m^3$ (Myrick, 1998).

Kindzierski and Sembaluk (2001) used passive monitoring techniques to measure seven-day average concentrations of SO_2 in indoor/outdoor air in two Alberta communities, Boyle (population 860) and Sherwood Park (population 42,000). Sherwood Park is a community adjacent to the Strathcona industrial corridor. Sampling occurred during a five-week period in late fall - a time of year when SO_2 is less reactive in the outdoor environment. Outdoor levels of SO_2 adjacent to 12 homes in Boyle (median: 4.3 $\mu g/m^3$, range: 3.7 to 5.6 $\mu g/m^3$) were two times lower than adjacent to 13 homes in Sherwood Park (median: 9.9 $\mu g/m^3$, range: 8.2 to 13 $\mu g/m^3$). Slightly higher indoor SO_2 levels were measured in Sherwood Park homes (median: 1.4 $\mu g/m^3$, range: 0.9 to 5.2 $\mu g/m^3$) than in Boyle homes (median: 0.5 $\mu g/m^3$, range: 0.2 to 2.3 $\mu g/m^3$). These results are consistent with characteristics of the two communities studied. Sherwood Park has many more SO_2–related emission sources than in Boyle (i.e. increased vehicle traffic and industrial emissions).

3.0 ATMOSPHERIC CHEMISTRY AND FATE

3.1 Sulphur Dioxide Removal Mechanisms from the Atmosphere

Once SO_2 is released into the atmosphere, it may be converted to other compounds and/or removed from the atmosphere by various mechanisms. Processes such as oxidation, wet deposition, dry deposition, absorption by vegetation and by soil, dissolution into water and other processes contribute to the removal of SO_2 from the atmosphere (ATSDR, 1998; Katz, 1977). SO_2 is therefore removed from the atmosphere either unchanged or in the form of sulphuric acid and sulphates (ATSDR, 1998). Hegg and Hobbs (1978) estimate that conversion of SO_2 to sulphuric acid and sulphates represents approximately 10% of the rate of removal of SO_2 from the atmosphere. According to Hegg and Hobbs (1978), the dominant processes for removal are washout (wet-deposition) and absorption. The following sections describe some of the significant removal mechanisms for SO_2 from the atmosphere.

3.1.1 Oxidation of SO_2

Oxidation of SO_2 in the atmosphere can occur homogeneously in the gas phase, homogeneously in the aqueous phase of raindrops, heterogeneously on the surfaces of particles or combinations of all three (Bunce, 1994; Finlayson-Pitts and Pitts, 1986). The rates of SO_2 oxidation processes are influenced by photochemistry and temperature (Finlayson-Pitts and Pitts, 1986). Photochemistry affects the rates of these oxidation reactions since some of the intermediate reactions may be photochemical in nature or some of the reacting species may be formed by photochemical reactions (Finlayson-Pitts and Pitts, 1986). Rates of oxidation of SO_2 are higher in the summer than in the winter and higher in midday that at night (Finlayson-Pitts and Pitts, 1986). The relative importance of the oxidation processes will be determined by the atmospheric conditions, specifically humidity and concentration and composition of particulate matter (Bunce, 1994). Table 3 provides a summary of these oxidation reactions.

Homogeneous gas phase oxidation of SO_2 involves three distinct mechanisms: (i) oxidation by photochemically generated reactive intermediates, (ii) oxidation by thermally generated reactive intermediates and (iii) direct photooxidation of excited SO_2 (Eggleton and Cox, 1978).

In considering the oxidation of SO_2 by photochemically generated reactive species, the most important oxidation reaction is the reaction of SO_2 with the hydroxyl radical (OH) (Bunce, 1994; Calvert and Stockwell, 1984):

$$SO_2 + OH \ (+ M) \rightarrow HSO_3 \qquad \text{Eq. 3.1}$$

where M is another molecule (N_2, O_2 or H_2O in air, for example) that serves to carry excess energy away from the reaction. Equation 3.1 results in a half-life for SO_2 of about 10 days and the formed HSO_3 radical eventually leads to the formation of sulphuric acid aerosol (Calvert and Stockwell, 1984). Many reaction pathways have been proposed for this conversion of HSO_3. The common pathway is given by the following two reactions (Bunce, 1994; Finlayson-Pitts and Pitts, 1986):

$$HSO_3 + O_2 \rightarrow SO_3 + HO_2 \quad \text{Eq. 3.2}$$

$$SO_3 + H_2O \rightarrow H_2SO_4 \quad \text{Eq. 3.3}$$

Other gas phase oxidation reactions include reaction with atomic oxygen (O), reaction with the Criegee biradical (RCHOOH) and reactions with other oxidizing species such as ozone (O_3), HO_2, and organic radicals (Bunce, 1994; Finlayson-Pitts and Pitts, 1986; Eggleton and Cox, 1978). These reactions are however negligible compared to the reaction with the OH radical, either due to slow reaction rates or low concentrations of reactive species under most atmospheric conditions (Bunce, 1994; Finlayson-Pitts and Pitts, 1986).

Table 3 Mechanisms of Conversion of Sulphur Dioxide to Sulphates (adapted from Wilson, 1978)

Mechanism	Overall Reaction	Factors affecting reaction
Direct Photooxidation	$SO_2 \rightarrow H_2SO_4$ (in the presence of light, oxygen and water)	Sulphur dioxide concentration; sunlight intensity
Indirect Photooxidation	$SO_2 \rightarrow H_2SO_4$ (in the presence of smog, water, NOx, organic oxidants, hydroxyl radical,…)	Sulphur dioxide concentration; organic oxidants, OH, HO_2 and RO radical concentrations
Oxidation in liquid droplets	$SO_2 \rightarrow H_2SO_3$ (in the presence of liquid water) $NH_3 + H_2SO_3 \rightarrow NH_4^+ + SO_4^{2-}$ (in the presence of oxygen)	Ammonia concentration
Homogeneous aqueous phase oxidation*	$SO_{2\,(aq)} \rightarrow$ sulphate (by dissolved H_2O_2, O_3, OH, SO_5^-, HSO_5^-, SO_4^-, PAN, CH_3COOH, $CH_3C(O)OOH$, HO_2, NO_3, NO_2, N(III), HCHO, Cl_2^-)	pH, ionic strength
Catalyzed oxidation in liquid droplets	$SO_2 \rightarrow SO_4^{2-}$ (in the presence of oxygen, liquid water and metal ions)	Metal ion or salt concentrations (Fe, V, Mn)
Catalyzed oxidation on dry surfaces	$SO_2 \rightarrow H_2SO_4$ (in the presence of oxygen, liquid water and metal ions)	Carbon particle concentration (surface area)

*Pandis and Seinfeld, 1989 as cited in Seinfeld and Pandis, 1998; Bunce, 1994

Oxidation of SO_2 by thermally generated reactive species involves reactions with alkenes (or olefins), N_2O_5 or NO_3. In the case of reactions with alkenes, it is suggested that due to the high concentrations of alkenes required for the reaction, oxidation of SO_2 via this mechanism would only occur in urban atmospheres or in industrial areas with sources of olefins. In the case of N_2O_5 and NO_3 reactions, results have shown that SO_2 is not oxidized to a measurable extent (Eggleton and Cox, 1978).

Direct photooxidation of SO_2 involves the reaction of excited SO_2 (SO_2 which has been excited by solar radiation (IARC, 1992)) with oxygen (O_2) to produce sulphur trioxide (SO_3). SO_3 then quickly reacts with water vapour to form sulphuric acid (H_2SO_4). Direct photooxidation is slow (Eggleton and Cox, 1978; Kellogg *et al.*, 1972) therefore this reaction is not considered to be an important pathway for the removal of SO_2 from the atmosphere (Kellogg *et al.*, 1972).

Homogeneous gas phase reactions lead to the production of H_2SO_4, which subsequently condenses either on to pre-existing particles or forms new particles with partial neutralization by NH_3 (Khoder, 2002). Through reaction with NH_3, H_2SO_4 is converted to $(NH_4)_2SO_4$ and/or NH_4HSO_4 (Khoder, 2002).

SO_2 is also removed from the atmosphere via catalytic oxidation of SO_2 in solution, either in cloud droplets, in fog, on moist surfaces of plants and soil, and at the surface of water bodies (Friend, 1973). This reaction can be written as (Friend, 1973):

$$SO_2 + \tfrac{1}{2} O_2 \text{ (dissolved)} + H_2O \rightarrow 2 H^+ + SO_4^{2-} \qquad \text{Eq. 3.4}$$

This reaction involves the dissolution of SO_2 into the aqueous solution to form H_2SO_3, which, in turn, is rapidly oxidized by molecular oxygen to form H_2SO_4. Examples of catalysts include NH_4^+ or certain transition metal ions in the form of salts (Friend, 1973; Kellogg, 1972). The catalysts may be present as part of the particulate matter present in the air and may serve as the nuclei on which the cloud drops form (Kellogg *et al.*, 1972).
According to Bunce (1994), oxidation of SO_2 in water droplets has been described since about 1985. This oxidation involves compound such as O_3, H_2O_2, NO_2 and others (Pandis and Seinfeld, 1989 as cited in Seinfeld and Pandis, 1998) but the mechanisms are uncertain (Bunce, 1994). These reactions are affected by parameters such as pH, ionic strength and temperature (Seinfeld and Pandis, 1998). Some modelling by Seinfeld and Pandis (1998) suggests that oxidation by dissolved H_2O_2 is predominant at pH values less than 4 or 5 and that oxidation by dissolved O_3 dominates at pH values above 5. Aqueous NO_2 oxidation of SO_2 under the studied conditions was negligible (Seinfeld and Pandis, 1998).

3.1.2 Wet and Dry Deposition

Wet deposition consists of two general processes, washout and rainout, with washout defined as all removal processes within clouds and rainout defined as removal by falling precipitation (Garland, 1978; Kellogg *et al.*, 1972). Washout processes, or processes responsible for the removal of SO_2 in clouds, include formation of sulphate particles (that serve as condensation nuclei), coagulation and diffusional uptake (HSDB, 2002). Rainout processes include interception of particles by falling raindrops and diffusional uptake of SO_2 (HSDB, 2002). Removal of SO_2 by wet deposition depends on a number of factors: precipitation type, intensity,

duration, frequency, relative amounts of SO_2 to sulphate, and the size distribution of particulate sulphate (HSDB, 2002).

Dry deposition refers to the direct collection of gaseous and particulate species on land or water surfaces (Garland, 1978). This direct transfer of SO_2 is believed to be the most important dry removal process for atmospheric sulphur (HSDB, 2002). Dry deposition of particles can occur directly onto plants, by gravitational settling or by physical or chemical capture of sulphate particles by moist surfaces (HSDB, 2002; Kellogg *et al.*, 1978).

Uptake of SO_2 by soil depends on the soil pH and moisture content (HSDB, 2002). SO_2 can also be absorbed directly from the air by plants (ATSDR, 1998).

With respect to the relative importance of wet and dry deposition, it has been suggested that both processes are important when considering larges areas. Dry deposition is however believed to be more important in areas closer to the source (HSDB, 2002).

Additional information on wet and dry deposition and more information on deposition in Alberta can be found in references such as Legge and Krupa (1990), Sandhu *et al.* (1986), AENV (1982) and Sandhu and Nyborg (1977).

3.2 Residence Time of SO_2 in the Atmosphere

The rate of the above mentioned removal processes combined with the rate of SO_2 emissions determine the residence time of SO_2 in the atmosphere. According to Katz (1977), the residence time of SO_2 in the atmosphere ranges from about 2 to 8 days. Hidy (1994) gives residence times of SO_2 in the lower atmospheres of 1 to 3 days. HSDB (2002) gives residence times ranging from 1 to 5 days.

4.0 EFFECTS ON LIVESTOCK AND WILDLIFE

Acute (single exposures) exposure to SO_2 produces immediate bronchial constriction, narrowing of the airways, increased pulmonary resistance, increased airway reactivity, and changes in metabolism. Chronic (continuous or multiple exposures) exposure results in swelling of the mucosal tissues and increased secretions (Lovati *et al.*, 1996, as cited in Coppock and Mostrom, 1997a; Amdur, 1991, as cited in Coppock and Mostrom, 1997a; WHO, 1979; Amdur, 1978). Ambient exposures may aggravate existing pulmonary diseases (Euler *et al.*, 1987, as cited in Mostrom and Campbell, 1987; Balmes *et al.*, 1987, as cited in Mostrom and Campbell, 1987; Linn *et al.*, 1987, as cited in Mostrom and Campbell, 1987). Impairment of lung function and reduced life span in humans has been attributed to long-term exposures to urban air pollution (Costa and Amdur, 1996; Heyder and Takenaka, 1996). The adverse effects associated with exposure to SO_2 seem worse with humid conditions (Heimann, 1961, as cited in O'Donohue and Graesser, 1962; McJilton *et al.*, 1973, as cited in WHO, 1979). In addition, respiratory effects may be aggravated by cold air (Heimann, 1961, as cited in O'Donohue and Graesser, 1962).

Sulphur Dioxide (SO_2) is one of a number of chemical and particulate constituents of air pollution and other industrial combustion emissions (Burns *et al.*, 1996; Costa and Amdur, 1996; Wellburn, 1998). For example with the right atmospheric conditions, SO_2 transforms into sulphuric acid; a chemical with more properties than SO_2 (Amdur *et al.*, 1978; Amdur, 1989, as cited in Scott, 1998; Gearhart and Schlesinger, 1989, as cited in Scott, 1998; Holma, 1989, as cited in Scott, 1998; Buštueva 1957, as cited in Lewis *et al.*, 1973). Sulphuric acid also binds to the surface of particulates in the air; the smaller the particulate, the greater the surface area and greater the ability to penetrate the lungs more deeply (Costa and Amdur, 1996). Sulphuric acid has been classified as a group 1 carcinogen by the International Agency for Research on Cancer (IARC, 1992, as cited in Scott, 1998).

There were only a few livestock and wildlife studies identified which reported effects of only. Most studies observed exposures to smoke/particulate matter and/or other gases in addition to SO_2. In these cases, it was difficult to clearly determine which constituent produced adverse health effects and what effects were synergistic (the result of concurrent exposures to a number of pollutants).

The focus of this assessment was ambient exposure to SO_2 only, and does not include assessment of exposure to sulphuric acid, airborne particulates, or chemical mixtures.

4.1 Overview of Chemical Disposition

Sulphur dioxide (SO_2) is a water soluble, irritant gas, which predominantly affects the upper airways. Penetration of the gas is greater with mouth breathing than with nose breathing, and with exercise (Skornik and Brian, 1990, as cited in Coppock and Mostrom, 1997a). The nose acts as a scrubber, removing SO_2 from the inhaled air before penetrating deeper into the airway (Costa and Amdur, 1996). Scrubbing by the upper respiratory tract appears to be more efficient at higher concentrations (40-53 mg/m^3; 15-20 ppm) (Amdur, 1978; Amdur, 1966 as cited in Coppock and Mostrom, 1997a, Amdur, 1978, and WHO, 1979). Extremely high exposures (concentrations were not defined) results in further penetration and significant damage of the

respiratory systems in experimental animals, or in some cases death, as the absorptive capacities of the upper airways are exceeded (WHO, 1979). Sulphur dioxide has been reported to remain in the lungs for up to one week or more (Balchum *et al.*, 1960a, as cited in WHO, 1979).

Once inhaled, SO_2 dissolves in the aqueous surfaces of the respiratory system as sulphite and bisulphite, which is absorbed into the cells in the respiratory tract and distributed through the body (Yokoyama *et al.*, 1971; Costa and Amdur, 1996; Wellburn, 1998). Studies involving inhalation of radiolabelled SO_2 reported the labelled ^{35}S was distributed by the blood throughout the body and was slowly eliminated (excretion was still observed hours after exposure had ended) (Yokoyama *et al.*, 1971; Bystrova, 1957, as cited in Yokoyama *et al.*, 1971 and WHO, 1979).

Sulphate oxidase (which occurs in the lung tissue as well as other body tissues) metabolizes sulphite and bisulphite into sulphates. Sulphite affects metabolic processes through inhibition of systemic enzymes (Khan *et al.*, 1987a, as cited in Khan and Schuler, 1997; 1987b, as cited in Khan and Schuler, 1997) including cells involved in the body's immune response (Wellburn, 1998). S-sulphonate products are also produced by metabolism of sulphite and bisulphite (Gunnison and Palmes, 1974; Yokoyama *et al.*, 1971). S-Sulphonated compounds were measured in rabbit tracheas and plasma (Gunnison *et al.*, 1981) and in human plasma (Gunnison and Palmes, 1974) after SO_2 inhalation. Whether S-sulphonates result in adverse systemic effects has not been determined (Costa and Amdur, 1996).

There are data to suggest that some individuals may be much more sensitive to exposures to sulphites due to a deficiency in the enzyme sulphite oxidase (Calabrese *et al.*, 1981; Wellburn, 1998; Hickey *et al.*, 1976; Warner *et al.*, 2000). Final metabolism occurs in the liver and excretion occurs via the urinary tract mostly in the form of inorganic sulphate (Balchum *et al.*, 1960a, as cited in Yokoyama *et al.*, 1971 and WHO, 1979; Balchum *et al.*, 1960b, as cited in WHO, 1979; Bystrova, 1957, as cited in Yokoyama *et al.*, 1971 and WHO, 1979; Frank *et al.*, 1967, as cited in WHO, 1979; Yokoyama *et al.*, 1971; Wellburn, 1998).

4.2 Genotoxicity and Carcinogenicity

Irritant gases may increase an animal's susceptibility to bronchial carcinoma (Costa and Amdur, 1996). Sulphite and bisulphite, produced in the respiratory tissue after inhalation of SO_2, are reactive nucelophiles (they are also the active ingredients formed after application of SO_2 when used as a food preservative) (Wellburn, 1998). In addition, both have a lone pair of electrons so oxidation can result in the production of free radicals, which may result in a number of adverse reactions including DNA chain cleavage (Wellburn, 1998).

In high concentrations sulphite (concentrations were not reported) are mutagenic (Wellburn, 1998). *In vitro* studies demonstrated that sulphite enhanced the mutagenic effects of benzo[a]pyrene (B[a]P), which led to speculation on whether SO_2 is a co-carcinogen for B[a]P (Reed and Jones, 1996). Gunnison *et al.* (1988) did not demonstrate SO_2 or systemic sulphite to be co-carcinogenic with B[a]P for occurrence of lung cancer in rats. IARC (1992 Abstract) reports there is limited or inadequate evidence of the carcinogenicity of sulphur dioxide and sulphites in experimental animals.

4.3 Acute Effects

Acute SO_2 exposure produces inflammation, oedema, and vascular changes. SO_2 is a pulmonary irritant targeting the upper respiratory tract and the lungs. Also affected are the mucus membranes of the eyes (Von Burg, 1995). Exposure may augment pulmonary allergic reactions, and increase susceptibility to bacterial infections (Matsumara, 1970a, as cited in WHO, 1979; Burns *et al.*, 1996; Selgrade and Gilmore, 1994, as cited in Burns *et al.*, 1996).

4.3.1 Acute Adverse Health Effects in Experimental Animals

Studies of experimental animals indicate that acute inhalation of SO_2 produces bronchioconstriction, increases respiratory flow resistance (due to the constriction of smooth muscle cells in the lung), increases the production of mucus, and has been demonstrated to reduce abilities to resist bacterial infection in mice (Costa and Amdur, 1996). Short exposures to low concentrations (<2.6 mg/m^3; <1.0 ppm) have been shown to have an immediate measurable physiological response (increases respiratory flow resistance) without resulting in significant or permanent damage to the respiratory system. In rabbits, acute exposure (16 mg/m^3 (6 ppm) for 4 hours) to SO_2 gas was irritating to the eyes and resulted in conjunctivitis, infection and lacrimation (Seiler, 1988, as cited in Von Burg, 1995). Short (30 min) exposures to concentrations up to 26 mg/m^3 (100 ppm) produced more significant respiratory changes in cats, which were usually completely reversible once exposure has ceased (Corn *et al.*, 1972). Similar results were reported in guinea pig experiments (Amdur, 1978).

Exposure to lethal levels of SO_2 (specific concentrations not provided) produced severe respiratory distress (coughing, laboured breathing, and rhinitis), eye irritation and conjunctivitis, and death (with pulmonary haemorrhaging, consolidation, and oedema) in experimental animal studies (animals not defined) (Amdur, 1978).

Amdur (1974, as cited in Amdur, 1978) reported that about 10% of subjects (both animal and human) responded with a heightened sensitivity (as indicated by higher pulmonary flow resistance) to SO_2 exposure. There were no distinguishing respiratory measurements before exposure that could identify potentially sensitive individuals.

Table 4 lists some examples of the lowest and highest No Observable Adverse Effect Levels (NOAELs) and Lowest Observable Adverse Effect Levels (LOAELs) reported in the literature.

Table 4 Examples of NOAELs and LOAELs Associated with Acute Sulphur Dioxide Exposure to Experimental Animals

Effects Reported	Exposure Period	Air Concentration ppm (mg/m^3)[a]	Species	Reference
Ocular-nasal irritation. LOAEL	8h	5 (13)	Swine	O'Donoghue and Graesser, 1962.
Pulmonary fibrosis LOAEL	8h	20 (53)	Swine	O'Donoghue and Graesser, 1962.
Reduced clearance of inert particles from the respiratory tract.	70 – 170 h	0.1, 1.0, 20 (0.26, 2.6, 5.3)	Rats	Costa and Amdur, 1996.
Impaired average daily weight gain. LOAEL	96h	10 (26)	Guinea pigs	O'Donoghue and Graesser, 1962.
10% increased flow resistance; decreased compliance. LOAEL	1h	0.16 (0.42)	Guinea Pigs	Amdur, 1966, as cited in Coppock and Mostrom, 1997a, Amdur, 1978, and WHO, 1979.
Increasing pulmonary resistance with increased dose.	1h	0.16–835 (0.46–2380)	Guinea pigs	Amdur, 1966, as cited in Coppock and Mostrom, 1997a, Amdur, 1978, and WHO, 1979.
Increased haemoglobin concentration. LOAEL	1h	6-310 (16-79)	Guinea Pigs	Lee and Danner, 1966, as cited in Yokoyama *et al.*, 1971.
Enhanced sensitization when exposed to an antigen after SO_2 exposure. NOAEL	30-50 min.	180 (510)	Guinea pigs	Matsumura 1970a, as cited in WHO, 1979.
Enhanced sensitization when exposed to an antigen after SO_2 exposure. LOAEL	30-50 min.	330 (940)	Guinea pigs	Matsumura 1970a, as cited in WHO, 1979.
Dyspnoeic attacks NOAEL	Unknown	400 (1100)	Guinea pigs	Matsumura 1970b, as cited in WHO, 1979.
Formation of S-sulphonate metabolites in tracheal tissue and plasma. LOAEL	3-24 h	3 (7.9)	Rabbits	Gunnison *et al.*, 1981.
Formation of S-sulphonate metabolites in tracheal tissue and plasma. LOAEL	1-72 h	10 (26)	Rabbits	Gunnison *et al.*, 1981.
Eye irritation. LOAEL	4h	6 (16)	Rabbits	Seiler, 1988, as cited in Von Burg, 1995.
Increasing pulmonary resistance with increased dose.	15-20 min.	7–230 (20–660)	Dogs	Frank and Speizer, 1965, as cited in WHO, 1979 and Costa and Amdur, 1996.
Increased pulmonary resistance flow. LOAEL		20 (53)	Cat	Corn *et al.*, 1972.

[a] When both units of concentration were not provided in the literature, the following conversion factor and assumptions were used: mg/m^3 x 24.45/MW =ppm; MW=64.06, air at 25°C and 101.3 kPa (760mmHg) (Plog *et al.*, 1996).

4.3.2 Acute Adverse Health Effects in Livestock

Sulphur dioxide can produce mild bronchial constriction, changes in metabolism, and irritation of the respiratory tract and eyes in cattle (Blood and Radostits, 1989a, as cited in Coppock and Mostrum, 1997a; Coppock and Mostrum, 1997a). An increase in airway resistance was reported in sensitized (allergic) sheep after four hours exposure to 5 ppm (13.25 mg/m^3) SO_2 (Abraham *et al.*, 1980).

In Europe, cattle deaths have been reported to occur after major incidents of air pollution (SO_2, sulphuric acid, and acid fog) (Schwabe, 1969; Prior and Lopez, 1992, as cited in Coppock and Mostrom, 1997a). Sulphur pollution associated with a coal-fired generating plant was associated with the death of a number of calves in Montana (Amber, 1978).

There have been anecdotal reports of adverse health effects occurring in cattle on farms near sour gas plants (Alberta Environmental Centre, 1996; Scott, 1998; CASA, 1999). However, these cases include exposure to a number of different chemicals, not just SO_2 and they may also represent conditions of concentrations that exceed typical ambient concentrations (e.g. conditions existing during sour gas well blowouts). There is currently a study underway in Alberta that is examining the potential health effects of gas plant emissions (including SO_2) on livestock health; the results are expected to be published in 2004 (WISSA, 2001).

4.4 Chronic Effects

4.4.1 Chronic Adverse Health Effects in Experimental Animals

Unlike acute exposures, chronic exposure does not appear to affect respiratory flow resistance. Adverse effects due to chronic exposure are caused by mucosal swelling and increased secretions (Ferin and Leach, 1973; Amdur, 1978). Studies of high concentrations demonstrated significantly impaired lung function and damage to the airways. Most long-term animal studies experimented with concentrations much greater than those expected with ambient exposures (26-1053 mg/m^3; 10-400 ppm). A few studies of exposures to concentrations more typical to ambient air concentrations also demonstrated adverse effects in pulmonary function.

Chronic exposure can affect mucus secretions and result in respiratory damage similar to chronic bronchitis (Amdur, 1978; Drazen *et al.*, 1982, as cited in Heyder and Takenaka, 1996; Seltzer *et al.*, 1984, as cited in Heyder and Takenaka, 1996; Shore *et al.*, 1987, as cited in Heyder and Takenaka, 1996; Scanlon *et al.*, 1987, as cited in Heyder and Takenaka, 1996; Bhaskar *et al.*, 1988, as cited in Heyder and Takenaka, 1996). Increased mucus secretion (due to increased number of mucus secreting goblet cells) and decrease ability of the cilia in the respiratory tract to beat, results in a reduced ability of the respiratory tract to clear particulates from the airways in rats and dogs (Amdur, 1978). These effects were reported at concentration above typical ambient concentrations (26-1053 mg/m^3; 10-400 ppm) (Dalhamn, 1956, as cited in Amdur, 1978; Reid, 1963, as cited in Amdur, 1978 and Costa Amdur, 1996; Lamb and Reid, 1968, as cited in Amdur, 1978; Chakrin and Saunders, 1974, as cited in Amdur, 1978; Spicer *et al.*, 1974, as cited in Amdur, 1978; Mawdesley-Thomas *et al.*, 1970, as cited in Amdur, 1978). However, Hirsch *et al.* (1975) (as cited in Amdur, 1978) demonstrated reduced particle clearance in dogs

exposed to low (2.6 mg/m^3; 1 ppm) concentrations and Ferin and Leach (1973) also demonstrated reduced particle clearance in rats when exposure (2.6 mg/m^3) exceeded 25 days.

Singh (1989) reported alterations in neonatal neuromuscular coordination after chronic maternal exposure (92 and 171 mg/m^3 (35 and 65 ppm) during days 7 to 18 of gestation) and a significant reduction in birth weight at day 1 in the higher exposure group. Table 5 lists some examples of the lowest and highest No Observable Adverse Effect Level (NOAELs) and Lowest Observable Adverse Effect Level (LOAELs) reported in the literature.

Table 5 Examples of NOAEL and LOAEL Associated with Chronic Sulphur Dioxide Inhalation for Experimental Animals

Effects Reported	Exposure Period	Air Concentration ppm (mg/m^3)[a]	Species	Reference
Thickening of mucus layer in trachea; decreased rate of mucus transport after cessation of exposure; increased number of goblet cells. LOAEL	18-67 days	10 (26)	Rats	Dalhamn, 1956, as cited in Amdur, 1978.
Increased haemoglobin concentration; increase white blood cell count and percentage neutrophils. LOAEL	Up to 13 months	1–31 (2.6-82)	Rats	Ball *et al.*, 1960, as cited in Yokoyama *et al.*, 1971.
Altered airway mucus secretion, goblet cell topography, or lung function. LOAEL	30 days	350 (921)	Rats	Reid, 1963, as cited in Amdur, 1978 and Costa and Amdur, 1996.
Increased number of mucus secreting cells. LOAEL	5h/day, 5d/week, 6weeks	300 (789)	Rats	Reid, 1963, as cited in Amdur, 1978 and Costa and Amdur, 1996.
Interstitial pneumonia, bronchitis, tracheitis, and peribronchitis. NOAEL	96 days	0.04 (0.1)	Rats	Elfimova and Gusev, 1969, as cited in WHO, 1979.
Interstitial pneumonia, bronchitis, tracheitis, and peribronchitis. LOAEL	96 days	0.18 (1.5)	Rats	Elfimova and Gusev, 1969, as cited in WHO, 1979.
Dose-response increased number of goblet cells. LOAEL	Ten 6h exposures	50 (132)	Rats	Mawdesley-Thomas *et al.*, 1970, as cited in Amdur, 1978.
Increased enzymatic activity in the alveolar macrophages. LOAEL	Ten 6h exposures	25 (66)	Rats	Mawdesley-Thomas *et al.*, 1970, as cited in Amdur, 1978.
Complete absence of Goblet cells.	Ten 6h exposures	300 (789)	Rats	Mawdesley-Thomas *et al.*, 1970, as cited in Amdur, 1978.
Decreased particle clearance. NOAEL	25 days	0.1 (0.26)	Rats	Ferin and Leach, 1973.
Decreased particle clearance. NOAEL	10-20 days	1 (2.6)	Rats	Ferin and Leach, 1973.
Decreased particle clearance. LOAEL	25 days	1 (2.6)	Rats	Ferin and Leach, 1973.
Decreased particle clearance. LOAEL	11 days	20 (53)	Rats	Ferin and Leach, 1973.
Changes in metabolism (increased plasma triglycerides, reduced high-density lipoproteins cholesterol. LOAEL	14 days	5 (13)	Rats	Lovati *et al.* 1996, as cited in Coppock and Mostrom, 1997a.
Reduced mean pup weight. NOAEL	Day 7-18 of gestation	32 (84)	Mice	Singh, 1989.

Table 5 Examples of NOAELs and LOAELs Associated with Chronic Sulphur Dioxide Inhalation for Experimental Animals (continued)

Effects Reported	Exposure Period	Air Concentration ppm (mg/m^3)[a]	Species	Reference
Delayed righting reflex on day 1 of birth; negative geotaxis on day 10 of birth. LOAEL	Day 7-18 of gestation	32 (84)	Mice	Singh, 1989.
Aerial righting score on day 12 of birth. NOAEL	Day 7-18 of gestation	32 (84)	Mice	Singh, 1989.
Increased susceptibility to respiratory bacterial infection. LOAEL	Up to 3 weeks	10 (26)	Mice	Azoulay-Dupuis *et al.*, 1982.
No pulmonary pathology. NOAEL	52 weeks	5.72 (15)	Guinea pigs	Alarie *et al.*, 1970.
Alterations in liver histology (hepatocyte vacuolation) (no changes in health of animals was observed). LOAEL	52 weeks	5.72 (15)	Guinea pigs	Alarie *et al.*, 1970.
No detrimental effects (body weight, growth, survival, pulmonary function, biochemical).	52 weeks	5 (13)	Guinea pigs	Alarie *et al.*,1975.
Initial increase of red blood cells which returned to normal.	10 months	100 (263)	Rabbits	Hayashi, 1956, as cited in Yokoyama *et al.*, 1971.
No Changes in haemoglobin and red blood cell concentrations. NOAEL	3.5h/day, 1.5 months	7 (20)	Rabbits	Volkova, 1960, as cited in Yokoyama *et al.*, 1971.
Altered airway mucus secretion, goblet cell topography, or lung function. LOAEL	225 days	5 (13)	Dogs	Lewis *et al.*, 1969, as cited in Amdur, 1978 and Costa and Amdur, 1996.
Haematological effects and lung histopathology. NOAEL	21 h/day, 620 days.	5.1 (13.4)	Dogs	Lewis *et al.*, 1973.
High mean nitrogen washout values. LOAEL	21 h/day, 620 days.	0.34 (0.9)	Dogs	Lewis *et al.*, 1973.
Squamous metaplasia; increased mucus goblet cells; increase mucus secretion. LOAEL	2 h, twice a week, 4-5 months.	500 (1316)	Dogs	Chakrin and Saunders, 1974, as cited in Amdur, 1978; Spicer *et al.*, 1974, as cited in Amdur, 1978.

Table 5 Examples of NOAELs and LOAELs Associated with Chronic Sulphur Dioxide Inhalation for Experimental Animals (continued)

Effects Reported	Exposure Period	Air Concentration ppm (mg/m³)[a]	Species	Reference
Slowed tracheal mucus transport. LOAEL	1 year	1 (2.6)	Dogs	Costa and Amdur, 1996.
No pulmonary pathology. NOAEL	78 weeks	1.28 (3.37)	Monkeys	Alarie *et al.*,1972 as cited in Amdur, 1978 and Costa and Amdur, 1996.
No detrimental effects (body weight, growth, survival, pulmonary function, biochemical). NOAEL	78 weeks	5 (13)	Monkeys	Alarie *et al.*,1975.
Pulmonary changes. NOAEL	1–6 weeks	35 (92)	Swine	Martin and Willoughby, 1971 as cited in Scott, 1998.

[a]When both units of concentration were not provided in the literature, the following conversion factor and assumptions were used: mg/m^3 x 24.45/MW =ppm; MW=64.06, air at 25°C and 101.3 kPa (760mmHg) (Plog *et al.*, 1996).

4.4.2 Chronic Adverse Health Effects in Livestock

A study of livestock (cattle, hogs, and chickens) exposed to SO_2 from a gas plant in the area, could demonstrate no adverse effects in animal health or productivity (McKinnon, Allen and Associates, 1977, as cited in Sandu *et al.*, 1980). This contradicted the assertions of the community (Sandu *et al.*, 1980).

In his PhD thesis, Scott (1998) examined the potential association between sour gas emissions and cattle health and productivity. Scott (1998) used historical data and computer exposure modelling to calculate levels of exposure and potential impact on cattle. Sulphur dioxide (SO_2) was used as surrogate marker for sour gas emissions. However, farms in the area of industry with high SO_2 emissions were also included in the study. There was no evidence of detrimental health effects in the dairy herds examined in association with sour gas plants or SO_2 emitting industries. One model demonstrated that in beef herds close to high SO_2 producing industry there *may be* an association between exposure and health effects in the beef herds (changes in the level of twinning and calving season profile); however, a strong association was not made (Scott, 1998).

Application of sulphur (no concentrations specified) to crops can decrease plant uptake of selenium (an essential nutrient for livestock), thus, deposition of sulphur dioxide *may* also affect the selenium content of forage plants (MacDonald and Klemm, 1973, as cited in Khan *et al.*, 1997; Frost and Ingvoldstad, 1975, as cited in Khan *et al.*, 1997; Gissel-Nielsen *et al.*, 1984, as cited in Khan *et al.*, 1997). Selenium deficiency can result in white muscle disease (lambs, goats, and cattle), in unthriftiness, reduced weight gains, diarrhea, neonatal weakness, reduced fertility, retained placenta, and abortions/stillbirths (cattle and sheep), and reduce immune

responsiveness (cattle, mice, rats, humans) (Trinder *et al.*, 1973, as cited in Khan *et al.*, 1997; Boyne and Arthur, 1979, as cited in Khan *et al.*, 1997; Boyne and Arthur, 1981, as cited in Khan *et al.*, 1997; Serfass and Ganther, 1975, as cited in Khan *et al.*, 1997; Taylor *et al.*, 1979, as cited in Khan *et al.*, 1997; Van Vleet, 1980, as cited in Khan *et al.*, 1997; McMurray and Rice, 1982, as cited in Khan *et al.*, 1997; Arvilommi *et al.*, 1983, as cited in Khan *et al.*, 1997; Maas, 1983, as cited in Khan *et al.*, 1997; Gyang *et al.*, 1984, as cited in Khan *et al.*, 1997; Petterson, 1985, as cited in Khan *et al.*, 1997; Yamini and Mullaney, 1985, as cited in Khan *et al.*, 1997; Boyne and Arthur, 1986, as cited in Khan *et al.*, 1997; Koller and Exon, 1986, as cited in Khan *et al.*, 1997; Smith *et al.*, 1988, as cited in Khan *et al.*, 1997; Rammell *et al.*, 1989, as cited in Khan *et al.*, 1997).

4.5 Adverse Health Effects in Wildlife

Air pollution has been attributed to the reduction and impairment of wildlife population, birds, mammals and insects (Lillie, 1970, as cited in Newman, 1979; Newman, 1975, as cited in Newman, 1979; Amber, 1978, as cited in Coppock and Mostrom, 1997a). It appears that exposure to air pollutants results in similar adverse effects in wildlife as laboratory and domestic animals (Newman, 1979). However, it is difficult to determine whether the effects reported are due to exposures to SO_2, other pollutants, or a combined exposure to SO_2 and other common air pollutants. Adverse effects on wildlife populations may be indirectly caused through effects of air pollution on availability of food resources and reduction of essential elements in forage (Newman and Schreiber, 1985).

Newman and Schreiber (1984) discuss effects of air pollution on ecosystems as well as the difficulty in determining specific adverse effects associated with specific air pollutants (due to the diversity of the pollution). They concluded that specific ecosystem properties (community energetics and structure, ecosystem life history, chemical cycling, ecosystem genetics, and homeostasis) have been adversely affected by air pollution.

In Czechoslovakia in 1971 exposure to SO_2 >0.15mg/m^3 (0.057 ppm) and fly ash (>300t/km^2/yr) produced hypocalcemia and hypoproteinesis in wild hares (Nováková and Roubal, 1971, as cited in Newman, 1979; Nováková *et al.*, 1973, as cited in Newman, 1979). Changes were also reported in the age distribution of hares in polluted areas; the ratio of young hares to old was significantly lower than in a control population (Nováková, 1969, as cited in Newman, 1979). Also in Czechoslovakia (in 1977) unreported concentrations of the same pollutants adversely affected nesting in house martins (Newman, 1977 as cited in Newman, 1979; Newman and Nováková, 1977 as cited in Newman, 1979). House martins appear to be a very sensitive indicator for industrial air pollution choosing unpolluted nesting areas (avoidance) over polluted areas during migration (Newman, 1979).

The Czechoslovakian studies also revealed a decrease in nematode infection of pheasants and hares in areas of heavy pollution (SO_2 and fly ash) (Nováková and Tremmolová, 1973, as cited in Newman, 1979) potentially due to adverse effects of the air pollution on the nematodes intermediate hosts (Nováková, pers. comm., as cited in Newman, 1979).

No adverse effects in moose density, productivity, or habitat utilization were identified in a two-year study of the animals living in the Whitecourt Forest area (Alberta) down wind of gas plants producing SO_2. Sulphur dioxide concentrations were not measured in this study, however, releases in the area were thought to be low (the average rarely exceeding 0.2 ppm; 0.52 mg/m^3), short (only minutes, rarely hours), and infrequent (Wride, 1975).

4.6 Infection Susceptibility

Exposure to SO_2 has been reported to increased susceptibility to both bacterial and viral infections (Fairchild *et al.*, 1972, as cited in Azoulay-Dupuis *et al.*, 1982; Selgrade and Gilmour, 1994 as cited in Burns *et al.*, 1996; Costa and Amdur, 1996). Azoulay-Dupuis *et al.* (1982) reported decreased resistance to bacterial infection in mice after exposure to high SO_2 concentrations (10 ppm; 26.5 mg/m^3).

5.0 EFFECTS ON MATERIALS

Building materials are subject to weathering decay (deterioration) under the action of meteorological factors such as precipitation, wind, and solar radiation. However, the presence of air pollutants – including acid aerosols and their precursors - can damage or accelerate the aging of building materials. Damage to building materials over time by exposure to sulphur pollution can represent a burden on the economy of industrialized nations (Nriagu, 1978). This damage can occur in the form of deterioration, corrosion, and staining. Annual deterioration losses to building materials in Canada due largely to sulphur compounds in the environment were estimated at $280 million in 1977 (Sereda, 1977).

Caution is warranted about estimating deterioration losses at present from this information because ambient sulphur concentrations have decreased since the 1970s such that the rates at which damage to materials occur would be expected to be less today. Building and building materials are located at ground level and are subjected to unique microclimatic conditions of each particular location with widely varying pollutant concentrations. Thus the effect of sulphur compounds on buildings would depend on actual amounts reacting with the surfaces of the materials.

The processes of deterioration, corrosion, and staining are complex phenomena governed by many factors (Sereda, 1977). In most cases, more than one process is involved, either simultaneously or sequentially. Vulnerable materials include stonework, selected metals (carbon steel, zinc, copper), and protective coatings (paint) (Kucera and Fitz, 1995; Longhurst *et al.*, 1993; Nriagu, 1978). Stainless steel and aluminum are considered to be more resistant metals (Longhurst *et al.*, 1993).

Table 6 lists the potential damaging effects of sulphur dioxide and other environmental factors to building materials (after Altshuller et al, 1983 as cited in Harter, 1986).

Table 6 Potential Sulphur Dioxide Damage to Building Materials

Material	Type of Impact	Other Environmental Factors
Building stone	Surface erosion	Mechanical erosion, cycles of relative humidity, temperature fluctuations, CO_2, microorganisms
Metals	Corrosion, tarnishing	Cycles of relative humidity, oxygen in air
Paints and organic coatings	Surface erosion, discoloration	Cycles of relative humidity, ultraviolet and visible light, mechanical erosion, O_3, microorganisms

After Altshuller *et al.* (1983) as cited in Harter (1986).

5.1 Delivery of Air Pollutants to Material Surfaces

There are several mechanisms in which air pollutants are transferred to material surfaces (Baedecker *et al.*, 1990; Sherwood, 1990). Wet deposition can occur as pollutants are delivered to surfaces of building, structures and objects by means of precipitation. Gases like SO_2 can dissolve in rain droplets and combine with water to form sulphuric acid. Dry deposition provides more of a continual delivery of pollutants, in the case of SO_2, as small (acidic) particles or as the precursor gas. Pollutants delivered by turbulent processes have the potential for attacking a greater portion of material surfaces than pollutants delivered by precipitation – for which sheltering can limit the surface aerial extent of deposition.

Critical factors influencing the deposition of gases and small particles to material surfaces are (after Longhurst *et al.*, 1993; Sherwood, 1990; Lipfert and Wyzga, 1986; Nriagu, 1978; Sereda, 1977):

Pollutant concentrations in air.

Turbulent (microclimatic) transfer processes (temperature, relative humidity, wind speed and direction, intensity and duration of rainfall).

Material configuration.

Presence of surface moisture.

Conditions of the material surface (e.g. surface chemistry, and porosity and microsurface roughness created by weathering).

In general, dry deposition rates increase under the following conditions (Sherwood, 1990; Edney *et al.*, 1989):

When pollutant concentrations in air are increased.

When turbulence is greater.

When the structural shape is more complex.

When the surface material has a greater chemical affinity for what is being deposited.

When the surface is wet (for soluble pollutants).

The chemistry of the material surface plays a major role in determining the dry deposition flux of pollutants (Sherwood, 1990). Alkaline materials (e.g. carbonate-containing stone) that can buffer surface moisture will tend to neutralize acidic pollutants more efficiently than other types of materials. Also, the presence of surface moisture significantly enhances dry deposition of SO_2 to all materials. Surface roughness on a microscale will tend to increase dry deposition as a larger surface area is created for transferring the pollutants. Therefore, as many materials weather, dry deposition will increase.

Wet deposition of acidity produced from precursor gases is enhanced by increased rain volume, particularly in summers when the highest airborne sulphate concentrations occur (Sherwood, 1990). Resuspension of alkaline dust (e.g. from unpaved roads, parking lots, construction areas) in urban centres tends to neutralize wet deposition of acidity.

5.2 Stonework and Concrete

Stonework. Stonework includes calcareous (carbonate-containing) stone, limestone, sandstone, and marble. Initially it is stated that stonework is subject to natural (mechanical, chemical – carbon dioxide, and biological) weathering and deterioration from anthropogenic processes (air pollution). The mechanical form of weathering occurs where minerals in rocks are deteriorated by wind, water and by particles transported by these two. Other mechanisms include cycles of wetting-drying and insulation weathering (Bland and Rolls, 1998):

Wetting-drying stress is an important process as it not only weakens rock, but also accelerates other processes. Water that enters pores and cracks cause these to expand and create stress in the rock. If a crack later dries up, water molecules may pull the crack together again. This means that the wetting-drying process creates a destructive cycle of expansion and contraction of a crack. This process also causes an increase in the size and numbers of the pores, explaining why this accelerates other processes.

Insulation weathering is a process by which changes in temperature create stresses on rocks. Simplified, it means that the sun heats rock surfaces causing expansion stresses. During nights the rock is under contraction stresses. This causes the rock to break if the amount of expansion/contraction is too high in relation to the elastic properties of the rock. This process is most important in climates where there are great temperature changes.

All of the processes described above deteriorate material surfaces naturally. Atmospheric sulphur compounds react with carbonates in stonework to form more soluble sulphur compounds such as calcium sulphate ($CaSO_4$), magnesium sulphate ($MgSO_4$), and calcium bicarbonate ($Ca(HCO_3)_2$) (Harter, 1986; Nriagu, 1978; Sereda, 1977). Water in the form of high relative humidity or as liquid water is always required for these reactions to occur. In addition, calcium carbonate ($CaCO_3$) is formed which may be removed or redeposited. $CaCO_3$ crystals are much larger and more porous, encouraging pollutant attack.

Dry deposited SO_2, unwashed by rainwater creates crusts on calcareous surfaces which, because of their heterogeneous and impervious nature, will cause underlying stone to become loose and flake off (Harter, 1986). Nriagu (1978) reported that much of the damage to building stone is attributable to the formation of these crusts. The crusts, aided by alternate freezing and thawing, cause blistering, scalding, exfoliation, and loss of cohesion of the surfaces. Essentially, the author reports that the stone may grow leprous because the conversion of carbonates to sulphates results in an increase in volume of crystallization. Granites, sandstones, and slates that do not contain calcareous cements are less susceptible to damage by sulphur pollution.

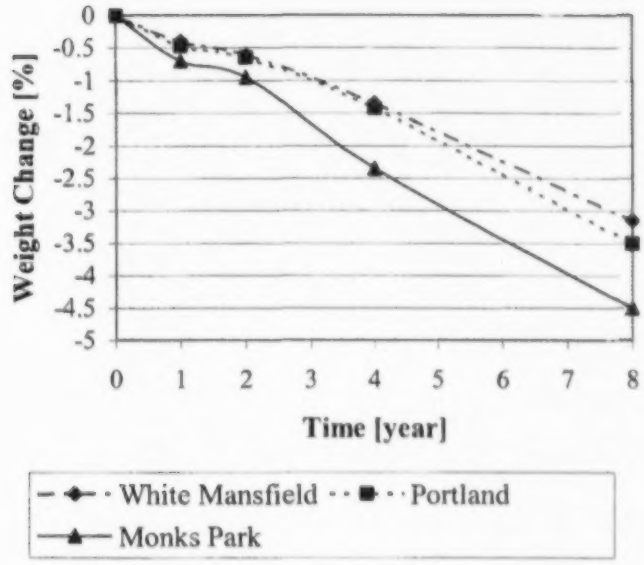
Physical measurements of the recession (erosion) of test calcareous stone surfaces exposed to ambient conditions at an angle of 30° to the horizontal was reported by Baedecker and Reddy (1993) and Baedecker *et al.* (1992) from five US National Acid Precipitation Assessment

Program (NAPAP) monitoring sites. Recession of the test stones ranged from 15 to 30 μm per year for marble and 25 to 45 μm per year for limestone. These were approximately double recession estimates based on the observed calcium content of run-off solutions from the test slabs.

Baedecker and Reddy (1993) and Baedecker *et al.* (1992) reported that erosion due to grain loss (loss of stonework grains at the surface) did not appear to be influenced by rainfall acidity and that evidence suggested that grain loss may be due to dry deposition of SO_2 between rainfall events. Chemical analysis of the run-off solutions and associated rainfall blanks suggested that approximately 30% of erosion by dissolution could be attributed to the wet deposition of hydrogen ion and the dry deposition of SO_2 and HNO_3 between rainfall events. The remaining 70% of erosion by dissolution was reported to be attributed to the solubility of the carbonate stone in rain that is in equilibrium with atmospheric carbon dioxide (i.e. clean rain).

The above trend reported by Baedecker and Reddy (1993) and Baedecker *et al.* (1992) is consistent with that estimated using a damage function by Lipfert (1989). Lipfert (1989) reported that 85% of surface loss to calcareous stone in the northeast US is due to the clean rain effect, 5% due to acid rain, and the balance (10%) due to gaseous SO_2 attack. Lipfert (1989) reported that experimental data on stone loss under more-or-less steady conditions, moderate SO_2 and particulate concentrations (i.e. relatively unpolluted circumstances) indicates that water is the most important agent for damage of calcareous stone.

Butlin *et al.* (1995, 1992a) reported on the results of a research program set up within the United Kingdom to investigate the effects of acidic deposition on buildings and building materials. At each of 31 sites, limestone and sandstone, mild steel, copper, aluminum, and galvanized steel were exposed, with some of the stone sheltered from direct precipitation. The research program – the National Materials Exposure Programme (NMEP) – was established in 1986. Stone tablets, 50 x 50 x 8 mm, were exposed on freely rotating carousels in sheltered and unsheltered (exposed) areas of buildings. Figure 1 indicates the weight loss behaviour of exposed stone samples at one of the NMEP sites over an eight-year period (after Butlin *et al.*, 1995).



After Butlin *et al.* (1995).

Figure 1 **Weight Losses of Exposed Stone Samples at National Materials Exposure Programme (NMEP) Site 14**

Spiker *et al.* (1995) undertook a laboratory chamber study of SO_2 dry deposition on limestone and marble. These authors reported that material surface variables (porosity, surface roughness, effective surface area) generally limit SO_2 dry deposition below about 70% relative humidity on limestone and below at least 95% relative humidity on marble.

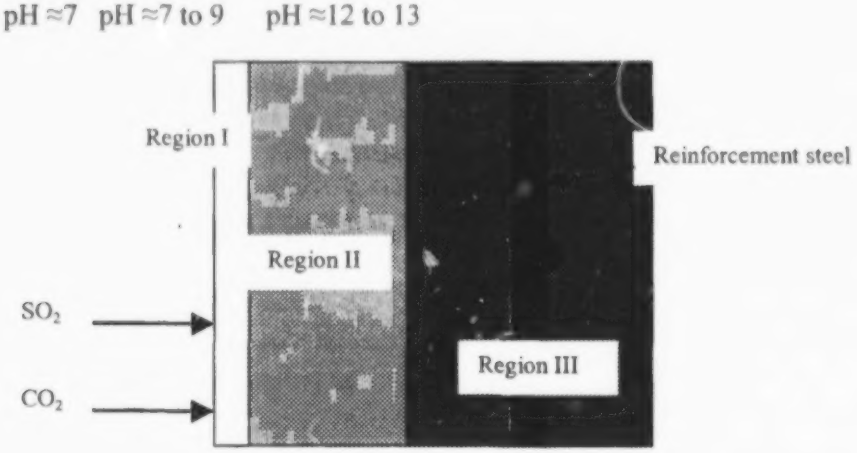
Delopoulou and Sikiotis (1992) undertook field experiments in Greece to compare the corrosive action of nitrates and sulphates on Pentelic marble with the action of gaseous NO_x and SO_2. These authors reported that the acids and their salts were more active than the corresponding oxides, despite the fact that the concentrations of the oxides in ambient air were much greater.

Concrete. Harter (1986) reported that little work has been done on the effects of acidic air pollutants on materials such as exposed concrete surfaces. Portland cement mortar and concrete are composed of stone aggregates along with silica (SiO_2), lime (CaO), alumina (Al_2O_3), iron (Fe_2O_3), and gypsum ($CaSO_4 \cdot 2H_2O$). Portland cement mortar and concrete are alkaline material (Harter, 1986) and are readily attacked by SO_2 and sulphate, with the hydrated calcium aluminate and/or calcium hydroxide component of the hardened cement paste being converted into ettringite (calcium sulphoaluminate hydrate) and gypsum (Nriagu, 1978).

Sereda (1977) reported that stresses associated with the substantial increase in the volume of crystallization (of ettringite and gypsum formation) may lead to a breakdown of the paste and

ultimately of the mortar or concrete. Longhurst *et al.* (1983) reported that calcium sulphite is formed after dry deposition of SO_2, combining with hydroxides present in the concrete.

Apart from the deterioration processes inherent in the quality of reinforced concrete (e.g. as a result of high chlorine content, high porosity, and alkali-silica reactions), Harter (1986) described potential processes involving air pollutant attack on concrete. In well-prepared concrete, the high alkalinity of the cement matrix (shown as Region III – non-carbonated zone – in Figure 2), protects reinforcement steel from corrosion. Loss of alkalinity and corrosion of the reinforcement steel occurs when the alkalinity is consumed by acidic species. A carbonated zone (Region II) exists as a result of the formation of calcium carbonate by the action of atmospheric CO_2. Reaction products of SO_2 attack (gypsum) remain at the surface (Region I) and can be washed away by rain on the wetted surface areas.



After Harter (1986).

Figure 2 Regions of Concrete Affected Differently by Attack from SO_2

Chlorides and, to some extent, nitrates are able to penetrate the carbonation zone (Region II) and even the unreacted zone (Region III). These will initiate corrosion of the reinforcement steel. Since corrosion products of steel occupy a greater volume than the original material, cracks will develop rendering the system open to attack by SO_2.

5.2.1 Damage Functions

In addition to developing an improved understanding of the basic processes during the study of deterioration of material surfaces, mathematical relationships of the rates of material loss are often sought. A dose-response (damage) function links the dose of pollution, measured in ambient concentration and/or deposition, to the rate of material weathering (deterioration, loss,

or corrosion). Damage functions must take into account the mechanics of delivery of the pollutants to the material surface and other factors that affect the loss process (e.g. temperature, moisture, etc.). Damage functions can be used to estimate the rate of material weathering. These functions can also be used to estimate economic (financial) losses from deterioration of material surfaces such as that reported by Sereda (1977) for annual deterioration losses to building materials in Canada due largely to sulphur compounds in the environment ($280 million in 1977).

Lipfert (1989) developed a damage function for generic calcite (calcium carbonate) stone deterioration valid for precipitation pH in the range of 3 to 5 using data from nine field exposure experiments in a statistical analysis:

$$\text{Annual surface loss/m rainfall} = [18.8 + 0.016H^{+}] + [0.18V_d \cdot SO_2/R] \qquad \text{Eq. 5.1}$$

Where,

H^+ = hydrogen ion concentration [mg/L],

V_d = deposition velocity [cm/s],

SO_2 = sulphur dioxide concentration [$\mu g/m^3$],

R = rainfall [m].

As indicated previously, Lipfert (1989) concluded that experimental data on stone loss under more-or-less steady conditions, moderate SO_2 and particulate concentrations (i.e. relatively unpolluted circumstances) and use of this damage function indicated that water is the most important agent for damage of calcareous stone.

ICP Materials. The International Co-operative Programme on Effects on Materials, including Historic and Cultural Monuments (ICP Materials, 2002) started in 1985 in Europe and Scandinavia. It was initiated in order to provide a scientific basis for new protocols and regulations developed within the Convention on Long-range Transboundary Air Pollution. The main aim of the ICP Materials exposure program is to perform a quantitative evaluation of the effects of multi-pollutants such as sulphur and nitrogen compounds, O_3 and particles as well as climate parameters on the atmospheric corrosion of important materials. Its primary objective is to collect information on corrosion and environmental data in order to evaluate dose/response (damage) functions and trend effects. This is achieved by exposing material specimens in a network of field test sites, by measuring gaseous pollutants, precipitation and climate parameters at or nearby each test site and by evaluating the corrosion effects on the materials.

Sweden serves as the lead country for the ICP Materials exposure program and the Swedish Corrosion Institute serves as the main research centre. Sub-centres in different European and Scandinavian countries are responsible for their own group of materials. All environmental measurements are reported and compiled by the Norwegian Institute for Air Research (NILU).

The results are useful for assessing acceptable corrosion rates and pollution levels, for mapping areas with elevated risk of corrosion damage and for calculation of corrosion costs.

Scientific experiments conducted by ICP Materials exposure program were designed to quantify damage to various materials by exposure to sulphur dioxide and acidic precipitation under varying environmental conditions. Some experiments were performed in the laboratory, where conditions such as pollutant concentration, temperature, relative humidity, wind speed and air turbulence could be controlled. Other experiments were performed at exposure sites in urban and rural environments. Data on materials damage and environmental conditions recorded at these sites were entered into a database for later analysis.

ICP Materials used data from these experiments to derive mathematical relationships between environmental factors and receptor materials. These relationships, known as damage functions, serve numerous uses (ICP Materials, 2002):

They contribute to an understanding of the cause-and-effect relationship between pollutants and observed damage.

They can be used to predict the remaining lifespan of culturally significant objects.

Policy makers can rely on damage functions to determine how air pollution regulations will affect materials within a specific region.

To date, the ICP Materials exposure program has tested a variety of materials, including calcareous stone and concrete, common structural metals, copper, bronze, glass, polymers at 39 sites in 12 European countries and in United States and Canada. With varying degrees of success, damage functions were determined for all materials studied. The results of ICP Materials exposure program not only confirm the corrosive effect of SO_2 but also enable quantification for a wide range of materials. For most unsheltered materials, wet deposition (acid precipitation) has also been quantified using results of the program and comprises the second most important contribution to the corrosion rate.

For unsheltered positions material damage is usually discussed in terms of dry and wet deposition. Wet deposition includes transport by means of precipitation and dry deposition transport by any other process. One important task for the ICP Materials exposure program has been to estimate the relative contribution of dry and wet deposition to the degradation of materials. Therefore, the dose/response functions for unsheltered materials are of the type (ICP Materials):

K = function of {dry deposition factors (T, Rh, $[SO_2]$, $[NO_2]$, $[O_3]$, t)}

+ function of {wet deposition factors (Rain, $[H^+]$, t)} Eq.5.2

Where,

K = corrosion attack (discussed below),

T = temperature [°C],

Rh = relative humidity [%],

[ ] = concentration of SO_2, NO_2 or O_3 [$\mu g/m^3$],

t = time [years],

Rain = amount of precipitation [mm],

[H+] = acidity of precipitation [mg/L].

The corrosion attack (K) can – depending on the material – be quantified as:

Surface recession (R, µm) for stone materials.

Mass loss (ML, g/m^2) for metals.

ASTM D 1150-55 rankings (1 to 10 where 10 means a fresh sample and 1 a completely degraded sample) for paint coatings.

Depth of leached layer (LL, nm) for glass.

A list of damage functions developed by ICP Materials from their eight-year field exposure program is provided in Table 7 for unsheltered limestone and sandstone.

Table 7 Damage Functions for Unsheltered Stoneworks Developed by ICP Materials

Material (N = number of observations, R^2 = explained variability) Dose-response (damage) function Temperature function
Portland limestone (N=100, R^2=0.88) $R = 2.7[SO_2]^{0.48}\exp\{f(T)\}t^{0.96} + 0.019Rain[H^+]t^{0.96}$ $f(T) = -0.018T$
White Mansfield sandstone (N=101, R^2=0.86) $R = 2.0[SO_2]^{0.52}\exp\{f(T)\}t^{0.91} + 0.028Rain[H^+]t^{0.91}$ $f(T) = 0$ when $T<10°C$, otherwise $-0.013(T-10)$

After ICP Materials (2002).

As indicated previously, atmospheric deterioration and corrosion of building materials is a cumulative, irreversible process, which proceeds even in the absence of air pollutants. The concept of acceptable deterioration (or corrosion) rates for building materials and ambient pollution levels that produce acceptable deterioration (or corrosion) rates has been proposed by ICP Materials (2002) and the UN ECE Convention on Long-range Transboundary Air Pollution (UN ECE, 2001). The acceptable corrosion rate should be determined by technical and economic considerations based on the specific application of a material. For model calculations, ICP Materials (2002) stated that for the purpose of comparing different materials with respect to

their pollution sensitivity, different levels of acceptance could be derived by relating the corrosion rate to rates in areas with "background" pollution.

UN ECE (2001) defined a dimensionless number, n, that relates the corrosion rate to corrosion rates in areas with "background" pollution:

$$n = K_{acc}/K_b \quad \text{Eq. 5.3}$$

where K_{acc} is the acceptable corrosion rate and K_b is the background corrosion rate.

The use of a specified acceptable corrosion rate in the damage function implicitly describes an acceptable multi-pollutant situation:

K_{acc} = function of {dry deposition factors (T, Rh, $[SO_2]$, $[NO_2]$, $[O_3]$, t)}

+ function of {wet deposition factors (rain, $[H^+]$, t)} Eq. 5.4

where the other parameters are described in Equation 5.2.

From Eq. 5.4, it is possible to reach an acceptable corrosion attack rate in several ways through a variety of combinations of parameter values (i.e. for temperature, relative humidity, pollutant level, etc.). Thus it is not possible to derive acceptable pollutant levels directly and uniquely. It is, however, possible to assess different scenarios based on reasonable assumptions for various parameters. The results of one example provided by ICP Materials (2002) is shown in Table 8 where it has been assumed that H^+ in precipitation (rain) is independent of the SO_2 level, which is not necessarily true. The acceptable SO_2 levels are based upon damage functions provided in Table 7 and using assumed values of an acceptable corrosion rate based on background.

Table 8 Ambient SO_2 Levels [$\mu g/m^3$] for Acceptable Stonework Deterioration Rates for Unsheltered Materials

Acceptable Corrosion Rate	Limestone	Sandstone
1.5·x background level	7	8
2.0 x background level	12	15

After ICP Materials (2002).

UK NMEP. The UK Nation Materials Exposure Programme developed damage functions for stonework based on empirical relationships of the form (after Butlin *et al.* 1995, 1992a):

$$\text{decay rate} = a(SO_2) + b(H^+) + c(\text{rainfall}) + d \quad \text{Eq. 5.5}$$

Where,

SO_2 = annual average atmospheric concentration [$\mu g/m^3$],

H^+ = rainfall acidity [g/m^2],

rainfall = total rainfall [mm].

A damage function developed by UK NMEP based on the first four-year field exposure data is provided in Table 9 for unsheltered calcareous stone (after Butlin *et al.* 1995, 1992a).

Table 9 Damage Functions for Unsheltered Calcareous Stonework Developed by UK NMEP

Material (R^2 = explained variability)	Exposure duration	Dose-response (damage) function
Calcareous stone (R^2=0.73)	4 years	Surface recession [mm] = $1.36[SO_2] + 0.0048[\text{rainfall}] + 29[H^+] + 8.4$

After Butlin *et al.* (1995, 1992a).

5.3 Metals

Corrosion of metals in the atmosphere is an electrochemical process that occurs through the formation of numerous complexes that act as electrochemical cells on the metal surface. Sulphur oxides merely modify and accelerate corrosion reactions that occur naturally when sufficient moisture is present on a metal surface (Sereda, 1977). The rate of metal corrosion is influenced by many factors relating to the type of metal, environmental variables, corrosion products, and time (Harter, 1986).

Atmospheric moisture is a critical controlling factor (Harter, 1986; Nriagu, 1978). In the absence of moisture, even high levels of sulphur compounds have little corrosive effect. Atmospheric corrosion is a discontinuous process with the result that the total corrosion damage is determined primarily by the percentage of time during which a critical humidity is exceeded. This is referred to as the "time-of-wetness" (Sereda, 1977).

Time-of-wetness is an estimated parameter based on the length of time that relative humidity is greater than a specified value (e.g. 80%) at a temperature greater than 0°C. It can be expressed as the hours or days per year or the annual percentage of time. Sereda (1974) developed a method for estimating time-of-wetness and reported that the fractions of total time during which the relative humidity exceeded 70, 80, 90, and 95% for continental Canadian locations were about 0.6, 0.4, 0.17, and 0.07, respectively.

Fogs and dews intensify material corrosion, because they cause the formation of surface films of water that can absorb gaseous pollutant from air (Nriagu, 1978). Longhurst *et al.* (1993) indicated that the role of precipitation in the corrosion of materials is more complex that a simple time-of-wetness relationship, since rainfall may exert a beneficial effect through its washing action. The effect of rainfall is complex because in the short-term it reduces the corrosion rate by diluting and washing away the corrosive material.

Over the long-term, however, it can enhance the corrosion rate by constantly stripping away the protective coatings from material surfaces. Air currents exercise considerable influence on the adsorption-desorption of SO_2 from condensed moisture films on material surfaces, and they affect the deposition of particulates and water droplets on materials (Nriagu, 1978).

Nriagu (1978) divided metals and their alloys into four broad groups on the basis of their susceptibility to attack by sulphur oxides:

Iron and ferroalloys, which are essentially non-resistant to attack.

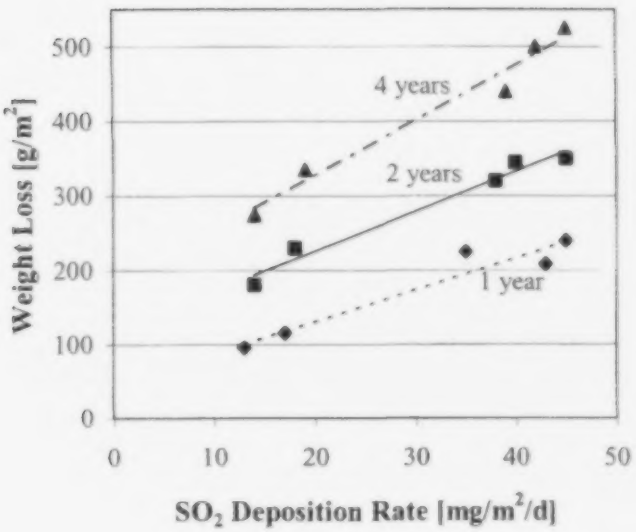
Metals resistant to attack in atmospheres with low levels of sulphur oxides. This group includes nonferrous metals such as cadmium, copper, nickel, and zinc.

Metals that readily attain a passive state and can withstand exposure to moderate levels of atmospheric sulphur pollution. This group includes chromium, aluminum, and other metals.

Nobel metals, which are essentially inert to sulphur oxides. This group includes gold, palladium, and platinum.

Steel. Carbon steel is not stable in water solutions but undergoes an oxidation reaction which is accelerated by the presence of acidic pollutants (Harter, 1986). Rusting may be initiated on the steel surface under hygroscopic deposits or at surface inclusions in the metal which dissolve when the surface becomes wet. The rust formed will absorb more atmospheric SO_2 and act as a catalyst in sulphate formation. This leads to formation of sulphate agglomerates, called sulphate nests, in the rust. When the surface becomes wet the sulphate nests act as anodes, in combination with the surrounding area that acts as the cathode to form corrosion cells.

Researchers have found that corrosion rates for carbon steels are well correlated with atmospheric SO_2. For example, total weigh loss for steel exposed to atmospheric SO_2 over one-, two-, and four-year periods is plotted in Figure 3 from different test sites in Sweden and Czechoslovakia (after Knotkova *et al.*, 1984 as cited in Harter, 1986). SO_2 deposition rates at these sites were reported to range from about 10 to 45 $mg/m^2/d$, which roughly corresponded to atmospheric concentrations ranging from 12 to 54 $\mu g/m^3$. Over four years, the corrosion rate at rural sites in Scandinavia with SO_2 levels less than 10 $\mu g/m^3$ was in the range of 11 to 13 μm per year.



After Knotkova *et al.* (1984), as cited in Harter (1986).

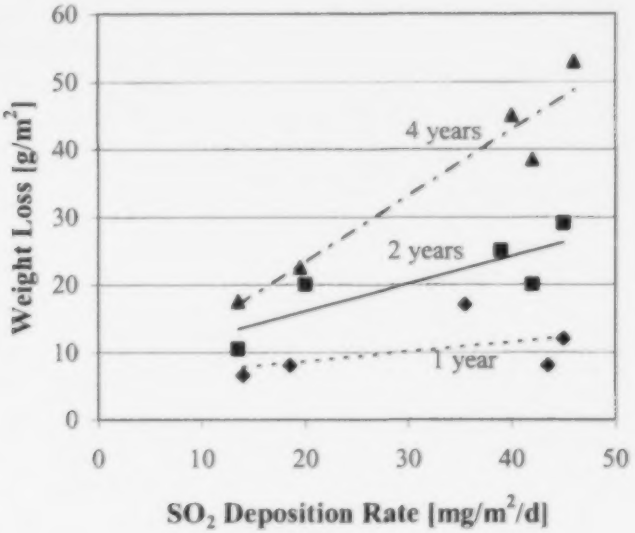
Figure 3 **Total Weight Loss of Steel with SO_2 at Sites in the Temperate Zone of Sweden and Czechoslovakia**

Zinc. Steel is used only with a protective coating such as paintwork or zinc galvanizing. Zinc provides both blanket protection to steel because of its lower corrosion rate and cathodic or galvanic protection to the steel after the integrity of the coating has been broken (Harter, 1986). In unpolluted air zinc reacts on contact with moisture to form zinc hydroxide, provided the pH is not too low. This in turn reacts with carbon dioxide in air and water to form a relatively insoluble and protective film of basic zinc carbonate.

When SO_2 is present the condensed moisture is acidic, and zinc corrodes rapidly. The corrosion products are soluble and dissolve and wash away, exposing the metal for the next contact with moisture. The principal factors controlling the rate of zinc corrosion are atmospheric SO_2 concentration, frequency of wetting, and the rate of drying of the material. Rainfall is not reported to be a serious contributor to high corrosion rates (Harter, 1986).

Figure 4 shows the relationship between total weight loss and zinc exposure to atmospheric SO_2 over one-, two-, and four-year periods at different test sites in Sweden and Czechoslovakia (after Knotkova *et al.*, 1984 as cited in Harter, 1986). The corrosion rate was much less than that for steel and was reasonably well correlated to the deposition rate. Knotkova *et al.* (1984) (as cited in Harter,1986) reported that these sites covered a range of time-of-wetness (i.e. relative humidity greater than 80% and temperature greater than 0°C) from 2,000 to 4,000 hours per year (or about 0.23 to 0.46 as a unitless fraction of time). Over four years, the zinc corrosion rate at rural sites in Scandinavia with SO_2 levels less than 10 $\mu g/m^3$ was in the range of 0.5 to 0.7 μm per year (compared to 4 to 13 μm per year for steel at the same sites).

Nriagu (1978) reported on the results of several long-term atmospheric exposure studies involving zinc and its alloys prior to 1975. These results generally showed that after an induction period of several months, corrosion rates attained a steady-state value that varied between 0.5 to 5 μm per year, depending upon the aggressiveness of the air pollutants. Caution is warranted about estimating corrosion rates for present conditions from these data because ambient sulphur concentrations have decreased since 1975 such that the rates at which corrosion to zinc occur would be less today.

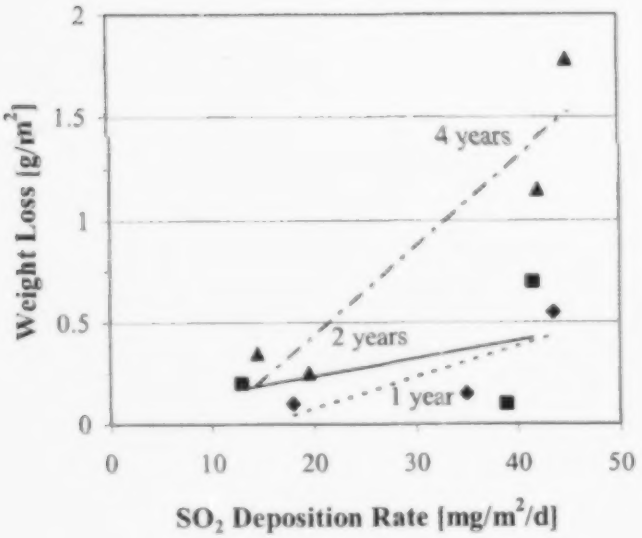


After Knotkova *et al.* (1984) as cited in Harter (1986).

Figure 4 Total Weight Loss of Zinc with SO_2 at Sites in the Temperate Zone of Sweden and Czechoslovakia

Aluminum. Aluminum and its alloys are used extensively for structural and architectural purposes. Most aluminum alloys have strong resistance to corrosion in mildly aggressive atmospheres (Nriagu, 1978). Aluminum surfaces form a thin dense oxide coating – which is highly protective – upon exposure to the atmosphere (Harter, 1986). The oxide coating is resistant to acidity down to pH 2.5, so it is protective to most SO_2 atmospheres. Although aluminum has good corrosion resistance, increasing SO_2 and NO_x concentrations accelerate corrosion. (Harter, 1986; Nriagu, 1978). Harter (1986) reports that corrosion rates tend to be less than 1 μm per year.

Figure 5 shows the relationship between total weight loss and aluminum exposure to atmospheric SO_2 over one-, two-, and four-year periods at different test sites in Sweden and Czechoslovakia (after Knotkova *et al.*, 1984 as cited in Harter, 1986). The corrosion rate is much less than that for steel and zinc.



After Knotkova *et al.* (1984), as cited in Harter (1986).

Figure 5 **Total Weight Loss of Aluminum with SO_2 at Sites in the Temperate Zone of Sweden and Czechoslovakia**

Copper. Copper tends to be used extensively as an architectural material because of its good corrosion resistance in pristine environments and its superior aging characteristics (Nriagu, 1978). SO_2 is only very mildly corrosive to copper at low relative humidity. However above a critical relative humidity, SO_2 attacks copper aggressively.

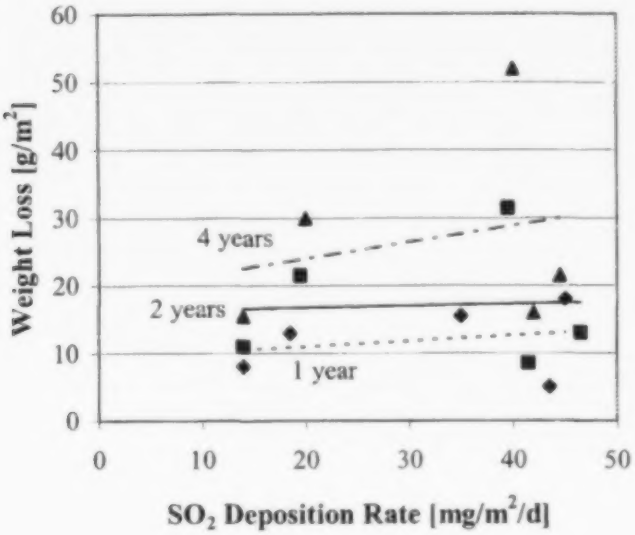
Figure 6 shows the relationship between total weight loss and copper exposure to atmospheric SO_2 over one-, two-, and four-year periods at different test sites in Sweden and Czechoslovakia (after Knotkova *et al.*, 1984 as cited in Harter, 1986).

On the basis of pre-1980 studies, Harter (1986) reported on general corrosion for a variety of copper-based metals in various types of atmospheres. It was reported that rates vary little, being 1 to 2.5 μm per year in industrial/urban environments and about 0.5 μm per year in rural environments.

Nriagu (1978) reported on the results of several long-term atmospheric sulphur exposure studies involving copper prior to the 1970s. The results generally showed that industrial/urban atmospheres had corrosion rates ranging from 0.9 to 2.2 μm per year and rural atmospheres had corrosion rates ranging from 0.1 to 0.6 μm per year. Nriagu (1978) did not indicate atmospheric SO_2 concentrations corresponding to these corrosion rates.

Caution is warranted about estimating corrosion rates for present conditions from the data presented by Harter (1986) and Nriagu (1978), particularly for industrial/urban atmospheres.

This is because ambient sulphur concentrations have decreased since the late 1970s such that the rates at which corrosion to copper occur would be less today.



After Knotkova *et al.* (1984), as cited in Harter (1986).

Figure 6 Total Weight Loss of Copper with SO_2 at Sites in the Temperate Zone of Sweden and Czechoslovakia

5.3.1 Damage Functions

ICP Materials. The International Co-operative Programme on Effects on Materials, including Historic and Cultural Monuments conducted scientific experiments to quantify damage to various metals by exposure to sulphur dioxide and acidic precipitation under varying environmental conditions (ICP Materials, 2002). A list of damage functions developed by ICP Materials from an eight-year field exposure program is provided in Table 10.

Again, from discussion presented in Section 5.2.1 and Eq. 5.4 it is possible to derive an acceptable corrosion attack rate in several ways through a variety of combinations of parameter values. These parameters include temperature, relative humidity, pollutant level, etc.

The results of one example provided by ICP Materials (2002) is shown in Table 11 where it has been assumed that H^+ in precipitation (rain) is independent of the SO_2 level, which is not necessarily true. The acceptable SO_2 levels are based upon damage functions provided in Table 10 and using assumed values of an acceptable corrosion rate based on a background rate. Here the background rate refers to corrosion rates occurring in areas with "background" pollution. For illustration purposes, Table 10 has shown acceptable SO_2 levels corresponding to 1.5 and 2 times the corrosion rates occurring in areas with background pollution.

Table 10 Damage Functions for Unsheltered Materials Developed by ICP Materials

Material (N = number of observations, R^2 = explained variability) Dose-response (damage) function Temperature function
Weathering steel (N=148, R^2=0.68) $ML = 34[SO_2]^{0.33}\exp\{0.020Rh + f(T)\}t^{0.33}$ $f(T) = 0.059(T-10)$ when T<10°C, otherwise $-0.036(T-10)$
Zinc (N=98, R^2=0.84) $ML = 1.4[SO_2]^{0.22}\exp\{0.018Rh + f(T)\}t^{0.85} + 0.029Rain[H^+]t$ $f(T) = 0.062(T-10)$ when T<10°C, otherwise $-0.021(T-10)$
Aluminum (N=106, R^2=0.74) $ML = 0.0021[SO_2]^{0.23}Rh\cdot\exp\{f(T)\}t^{1.2} + 0.000023Rain[Cl^-]t$ $f(T) = 0.031(T-10)$ when T<10°C, otherwise $-0.061(T-10)$
Copper (N=95, R^2=0.73) $ML = 0.0027[SO_2]^{0.32}[O_3]^{0.79}Rh\cdot\exp\{f(T)\}t^{0.78} + 0.050Rain[H^+]t^{0.89}$ $f(T) = 0.083(T-10)$ when T<10°C, otherwise $-0.032(T-10)$
Cast Bronze (N=144, R^2=0.81) $ML = 0.026[SO_2]^{0.44}Rh\cdot\exp\{f(T)\}t^{0.86} + 0.029Rain[H^+]t^{0.76} + 0.00043Rain[Cl^-]t^{0.76}$ $f(T) = 0.060(T-11)$ when T<11°C, otherwise $-0.067(T-11)$
Coil coated galvanized steel with alkyd melamine (N=138, R^2=0.73) $(10\text{-ASTM}) = (0.0084[SO_2] + 0.015Rh + f(T))t^{0.43} + 0.00082Rain\cdot t^{0.43}$ $f(T) = 0.040(T-10)$ when T<10°C, otherwise $-0.064(T-10)$
Steel panels with alkyd (N=139, R^2=0.68) $(10\text{-ASTM}) = (0.033[SO_2] + 0.013Rh + f(T))t^{0.41} + 0.0013Rain\cdot t^{0.41}$ $f(T) = 0.015(T-11)$ when T<11°C, otherwise $-0.15(T-11)$
Glass M1 representative of medieval stained glass windows (N=46, R^2=0.56) $LL = 0.013[SO_2]^{0.49}Rh^{2.8}t$

After ICP Materials (2002).

Table 11 Ambient SO_2 Levels [µg/m^3] for Acceptable Corrosion Rates for Unsheltered Metals

Acceptable Corrosion Rate	Weathering steel	Zinc	Aluminum	Copper	Bronze
1.5 x background level	5	12	10	7	5
2.0 x background level	45	29	39	33	12

After ICP Materials (2002).

UK NMEP. The UK Nation Materials Exposure Programme also developed damage functions for metals based on empirical relationships in the form of (after Butlin *et al.* 1995, 1992b):

$$\text{Surface recession [mm]} = a(SO_2) + b(R) + c \quad \text{Eq. 5-6}$$

Where,

SO_2 = annual average atmospheric concentration [mg/m^3],

R = total rainfall for exposure period [mm].

Damage functions developed by UK NMEP based on the first four-year field exposure data are provided in Table 12 for unsheltered metals (after Butlin *et al.* 1995, 1992b).

Table 12 Damage Functions for Unsheltered Metals Developed by UK NMEP

Material (R^2 = explained variability) Exposure duration Dose-response (damage) function
Mild steel (R^2=0.76) 4 years Surface recession [mm] = $1.9[SO_2] + 0.012[R] + 41$
Copper (R^2=0.41) 4 years Surface recession [mm] = $0.025[SO_2] + 0.0037[R] + 2.2$
Aluminum (R^2=0.43) 4 years Surface recession [mm] = $0.012[SO_2] + 0.00018[R] + 0.72$
Galvanized steel (R^2=0.85) 2 years Surface recession [mm] = $0.077[SO_2] + 0.0011[R] + 1.7$

After Butlin *et al.* (1995, 1992b).

5.4 Paints

Paints consist of pigment, additives, and a vehicle fluid holding the pigments and additives in suspension (Harter, 1986). The most important factors in the deterioration of paint films are ultraviolet light and atmospheric oxidants, including oxygen and wetness (Altshuller *et al.*, 1983 as cited in Harter, 1986). Sulphur dioxide affects paints in two principal ways (Nriagu, 1987): (1) by increasing the drying time of the paint film, and (2) by attacking the mature dry film, causing loss of gloss.

Edney *et al.* (1988) and Igetoft (1985) reported that corrosion on a painted steel surface generally starts at defects in the coating, where ionic species can reach the metal surface and stimulate anodic dissolution of metal. The degree of spreading of the corrosion reactions around a defect is reported to depend on several factors (type of surface preparation, coating material, and environment factors). The first step in this spread is a loss of coating adhesion through cathodic delamination. Igetoft (1985) stated that sulphur dioxide is a common corrosion stimulator and that exposure in sulphur dioxide environments tends to give a neutral to acid subcoating liquid. Depending on the properties of the bonds between paint vehicle and substrate (steel), different effects may be expected.

Sereda (1977) and Nriagu (1987) report that little is known about the effects of sulphur pollution on latex paints. Harter (1986) indicated that there are so many different types of paints and each has many and varied competing formulations for both pigment and vehicle fluids. Furthermore, the effect of atmospheric pollutants may vary with the formulation and the formulation can vary over the lifetime of any brand of paint. This makes long-term testing of paint films difficult, and reliable data on exposure-response relationships are limited.

Sereda (1977), Harter (1986), and Igetoft (1985) indicate that repainting intervals for exterior surfaces are generally shorter in urban atmospheres compared to rural atmospheres. For example, Sereda (1977) reported that the expected surface life of paint on urban households is only three years as compared to six for rural households.

6.0 AIR SAMPLING AND ANALYTICAL METHODS

6.1 Reference Methods

Air sampling and analytical methods for sulphur dioxide that are used in practice by established agencies are reported. In general, standard air monitoring methods for sulphur dioxide are based on direct manual and automatic sampling technologies or integrated pump-and-tube and filter pack sampling approaches. Widely employed and accepted reference air monitoring methods and technologies for sulphur dioxide have been developed, tested and reported by the United States Environmental Protection Agency (US EPA), National Institute of Occupational Safety and Health (NIOSH), and Occupational Safety and Health Administration (OSHA). Table 13 provides a description of individual method advantages and disadvantages.

6.1.1 US EPA Reference Method

The US EPA reference method for the determination of sulphur dioxide in the atmosphere is a colourimetric procedure based on a modified version of the pararosaniline method originally developed by West and Gaeke in 1956 (US EPA, 1982). This is a manual method in which a measured volume of air is bubbled through a solution of potassium tetrachloromercurate (TCM). The sulphur dioxide present in the air stream reacts with the TCM solution to form a stable monochlorosulfonatomercurate complex. Once formed, this complex resists air oxidation and is stable in the presence of strong oxidants such as ozone and oxides of nitrogen.

During subsequent analysis, the complex is reacted with acid-bleached pararosaniline dye and formaldehyde to form an intensely coloured pararosaniline methyl sulfonic acid. The optical density of this species is determined spectrophotometrically and is directly related to the amount of sulphur dioxide collected. The total volume of air sampled, corrected to US EPA reference conditions (25°C, 760 mmHg), is determined from the measured flow rate and the sampling time. The concentration of sulphur dioxide in the ambient air is subsequently computed and expressed in micrograms per standard cubic meter ($\mu g/m^3$).

The lower limit of detection of sulphur dioxide with this technique is approximately 25 $\mu g/m^3$ (0.01 parts per million (ppm)) in an air sample of 30 litres (L) and 13 $\mu g/m^3$ (0.005 ppm) in an air sample of 288 L. Advantages of this technique are that it is specific for sulphur dioxide, it uses a simple and inexpensive apparatus, and it is suitable for sampling periods from 30 minutes to 24 hours. Disadvantages are that samples must be analyzed soon after collection and there are possible interferences from oxides of nitrogen and some metals. Other disadvantages include a relatively slow response time, the need for frequent periodic maintenance and the required use of wet chemical reagents.

6.1.2 US EPA Manual Equivalent Methods

US EPA equivalent methods used to monitor sulphur dioxide in the atmosphere must be capable of generating data comparable to data generated using the reference method. The monitoring systems designated as manual equivalent methods by the US EPA are colourimetric analyzers that use various modifications of the pararosaniline method described above. The two monitors

are the Technicon I Automated Analysis System and the Technicon II Automated Analysis System (US EPA, 2002). Both analyzers consist of an absorber column, a gas liquid separator, a mixing coil, and a flow-through colourimeter with a narrow band optical filter. The major difference between these analyzers and the reference method is that they can be operated continuously.

The advantages of using these continuous colourimetric analyzers are they provide good sensitivity and specificity. In addition, data collected using these analyzers have a very good probability of correlating with data collected using the US EPA reference method because both methods are based on the same colourimetric principle. The disadvantages of using these analyzers are the relatively slow response time, the need for frequent periodic maintenance and the use of wet chemical reagents.

6.1.3 US EPA Automated Equivalent Methods

Several different measurement principles have been utilized for constructing commercially available continuous monitors used to determine ambient concentrations of sulphur dioxide (WHO, 1999; ARPEL, 1998). These measurement principles include: ultraviolet fluorescence, flame photometric detection, gas chromatography with flame photometric detection, colourimetry, infrared absorption and coulometry. The US EPA has designated an number of commercial monitors based on these principles as automated equivalent methods for determining ambient concentrations of sulphur (US EPA, 2002). Refer to Table 14 for a list of the US EPA designated automated equivalent methods for continuous monitoring of sulphur dioxide.

6.1.3.1 Ultraviolet Fluorescence

This method is based on the characteristic fluorescence by the sulphur dioxide molecule when it is irradiated by ultraviolet light (Okabe *et al.*, 1973). This fluorescent light is also in the ultraviolet (UV) region of the spectrum but at a different wavelength than the incident radiation. By monitoring the fluorescent wavelengths between 190 and 230 nm, there is very little quenching of the fluorescence by other components in the air. The light is detected with a photomultiplier tube producing a voltage proportional to the light intensity that is translated to concentrations by means of calibration factors. Either a continuous mechanically chopped or electronically pulsed UV light source is used. Instruments employing electronically pulsed UV light sources may cost more initially, but the pulsed UV light source lifetime is longer. Both water vapour and oxygen strongly quench the sulphur dioxide fluorescence at specific wavelengths. Water vapour may be removed with a permeation drier, although interference can be avoided by properly selecting the light sources and the optical filter. The effect of oxygen quenching is minimized by maintaining identical oxygen levels in calibration and sample gases. Polycyclic aromatic hydrocarbons exhibit strong fluorescence in the same spectral region as sulphur dioxide and may be removed by ambient or elevated temperature scrubbers. However, some aromatic scrubbers randomly allow breakthrough (Smith and Buckman, 1981). Advantages of the UV fluorescence analyzers for sulphur dioxide are high accuracy and low detection limits (usually 2 to 5 $\mu g/m^3$; 1 to 2 parts per billion (ppb)).

6.1.3.2 Flame Photometric Detection

Flame photometric detection (FPD) is highly specific for sulphur compounds and is used to measure airborne sulphur dioxide. In FPD analyzers, the discrete light emission is measured from excited sulphur molecules after passing through a reducing-hydrogen flame. The emitted light is optically filtered to detect the specific 394 nm sulphur band with a photomultiplier tube. Typically, continuous FPD based sulphur dioxide analyzers have detection limits of 5 $\mu g/m^3$ (2 ppb), a lag time of 3 seconds, and a 10-second response time. Advantages of FPD systems include low maintenance, high sensitivity, very fast response and good selectivity for sulphur compounds (PACE, 1985). A disadvantage of the FPD systems includes the need for a compressed hydrogen source or hydrogen generator. In addition, although the FPD is insensitive to most non-sulphur species, it will detect sulphur compounds other than sulphur dioxide. Since the concentration of H_2S, mercaptans, and other organic sulphur compounds in typical urban air is less than 10 % of sulphur dioxide levels the potential interference is minimal. Particulate filters remove aerosol sulphates and other particulate matter to eliminate clogging and light scattering. Selective filters are available to reduce interference from other sulphur compounds (e.g. an H_2S filter for commercial instruments).

6.1.3.3 Gas Chromatography With Flame Photometric Detection

Gas chromatographs with flame photometric detectors (GC-FPD) are available commercially. An optimized chromatographic column is used to separate various sulphur compounds (i.e., COS, H_2S, CS_2, sulphur dioxide and RSH). The separated compounds are subsequently detected and quantified with the FPD. Typical detection limits for these systems are about 2 to 3 $\mu g/m^3$ (1 ppb). Since compounds are separated by chromatography, measurements exhibit greater specificity and less bias due to interfering compounds than simple FPD systems. However, hydrocarbons may bias the results due to quenching effects if the hydrocarbon has the same retention time and is present at high concentrations (PACE, 1985). Major disadvantages of GC-FPD systems are the need for compressed hydrogen gas, the need for highly trained technicians and the lack of continuous results since samples require up to 6 minutes to process.

6.1.3.4 Colourimetry

Colourimetric analyzers are based upon the reaction of sulphur dioxide with solutions of organic dyes to form coloured species. Optical absorbance of the coloured complex in solution, measured spectrophotometrically, is linearly proportional to the concentration of the coloured species according to Beer's Law. Several examples of colourimetric methods for determining sulphur dioxide are described below.

The pararosaniline method developed by West and Gaeke (1956) has been automated for monitoring sulphur dioxide in ambient air. Not only has this automated method been used by the US EPA, as mentioned earlier, but its use has also been suggested by a number of other agencies (e.g. Canadian Environmental Protection Service report no. EPS-1-AP-72-4 and ASTM "Standard Test Method for Sulphur Dioxide Content of the Atmosphere" method no. D2914-01) (ARPEL, 1998). In this method, sulphur dioxide is absorbed by aspirating a measured volume of air through a tetrachloromercurate (TCM) solution, resulting in the formation of a complex. EDTA is added to remove heavy metal interferences. Pararosaniline, formaldehyde and the

sulphur dioxide complex react to form an intensely coloured pararosaniline methyl sulphonic acid that is analyzed spectrophotometrically.

The signal is translated to the sulphur dioxide concentration in the air sample by means of calibration data. Automation of the West-Gaeke method is rarely practical for continuous monitoring since some solutions require daily preparation. Typical features of some commercially available instruments are detection limits of approximately 13 $\mu g/m^3$ sulphur dioxide (5 ppb), lag time of 2 minutes and response time of 3 minutes. Advantages of these instruments include simplicity, high sensitivity and, with proper control, good specificity. Interferences by nitrogen oxides may be controlled by using a sulfamic acid reagent. Heavy metals may be complexed with EDTA in the scrubbing solution or with phosphoric acid in the dye solution. Ozone interference may be controlled by the use of a delay coil downstream of the absorber to allow time for ozone to decay, but this results in longer lag and response times. Major disadvantages of these instruments are the need for reagent and pump tubing replacement and frequent recalibration.

Iodometric colourimetric analyzers employ regenerative chemical cartridges and detection by spectrophotometry. A sodium iodide solution passes through a reference cell to a set of electrodes generating iodine by electrolysis. The amount of iodine is reduced by reaction with sulphur dioxide in the sample stream and the reduction is measured spectrophotometrically. The iodine is regenerated to iodide in solution by a regenerative cartridge. The most sensitive operating range for this instrument is 5 to 500 $\mu g/m^3$ (2 to 200 ppb). Oxidizing gases interfere to give low results; reducing agents interfere to give high results. Interference from high concentrations of nitrogen oxides or ozone can be removed by introducing hydrogen into the air sample and passing the mixture over a platinum catalyst at 100°C.

6.1.3.5 Infrared Absorption

Fourier transform-infrared analyzers (FT-IR) with path lengths of 1 km or more have been designed to monitor a wide range of pollutants in ambient air including sulphur dioxide, CO, NO, NO_2 and O_3. This method is based on absorption of incident electro-magnetic radiation at characteristic infrared wavelengths by sulphur dioxide across long distances. By monitoring the magnitude of infrared light absorption by sulphur dioxide over the path length, sulphur dioxide can be detected at low ppb levels. Computerized Fourier transformations of the absorption signals are used to separate the sulphur dioxide signals from instrumental noise by superimposing repetitive infrared scans until an absorption peak is resolved. A Michelson interferometer modulates the absorption frequency range so it can be measured. The application of infrared absorption to the monitoring of sulphur dioxide in ambient air has not yet gained wide acceptance as a routine monitoring method.

6.1.3.6 Coulometry

Coulometric analyzers are based on the reaction of sulphur dioxide with a halogen, formed directly by electrolysis of a halide solution. Typically, an inner chamber (into which air samples are introduced) is contiguous with an outer chamber. Both contain solutions of potassium bromide and bromine in dilute sulphuric acid. The potential difference between the chambers, relative to a reference potential, is measured by the reference electrodes. As absorbed sulphur

dioxide reduces the bromine in the inner chamber, the amplifier produces a current to restore the bromine until the potential difference returns to zero. The current needed to replace the depleted halogen is proportional to the amount of sulphur dioxide absorbed in solution, and hence to the sulphur dioxide concentrations.

The major advantages of using coulometric instruments are good sensitivity, minimal maintenance (reagent consumption is negligible since halides are regenerated and evaporated water is replaced by condensation from air or from a reservoir), and simplicity of operation. The major disadvantage of using this technique is the necessity of using selective filters to eliminate interfering species. Interfering species are those that oxidize halides, reduce halogens, or complex with either. They consist primarily of sulphur compounds (i.e., H_2S, mercaptans, and organic sulphides, disulphides) with sensitivities comparable to that of sulphur dioxide. Other, less important interferences are O_3, NO_x, chlorine, ethylene, aldehydes, benzene, chloroform, other nitrogen or halogen-containing compounds, and other hydrocarbons. Interferences can be minimized by selective filters such as heated silver gauze filters to remove H_2S, O_3, NO_x, chlorine, carbon disulphide, ethylene, aldehydes, benzene, and chloroform, but will not remove mercaptans.

6.1.4 NIOSH Method 6004

In addition to the reference and equivalent air monitoring methods for sulphur dioxide developed by the US EPA, both the NIOSH and OSHA have also developed methods for sulphur dioxide that are suitable for occupational, personal and area monitoring. The current methodology used by the NIOSH to determine sulphur dioxide in air (NIOSH Method 6004) consists of collecting sulphur dioxide on a treated filter, desorbing with a solution of $NaHCO_3$ and Na_2CO_3 and analyzing by ion chromatography (NIOSH, 1994). Sampling is conducted by drawing air through a filter pack containing two 37 mm diameter cassette filters using a personal sampling pump calibrated to within 5% of the recommended flow rate. The first filter is used to collect and remove particulate sulphate interferences. The second filter, which has been treated with a solution of Na_2CO_3, is used to collect the sulphur dioxide. The suggested flow rate is between 0.5 and 1.5 L/min and the recommended volume collected is between 40 and 200 L. The working sulphur dioxide concentration range for this method is 0.2 to 8 ppm (0.5 to 20 milligrams per cubic meter (mg/m^3)) for a 100 L sample.

6.1.5 OSHA Method ID-104

The OSHA currently has two acidimetric methodologies for the determination of sulphur dioxide in air. OSHA Method ID-104 consists of using a personal sampling pump to draw a known volume of air through a midget-fritted glass bubbler containing a solution of hydrogen peroxide (OSHA, 1989). The hydrogen peroxide converts the sulphur dioxide in the air to sulphuric acid, which is subsequently analyzed as sulphate using a slightly basic eluent and an ion chromatograph equipped with a conductivity detector. The amount of sulphate is gravimetrically converted to represent the amount of sulphur dioxide collected. Advantages of this method include: adequate sensitivity for measuring workplace atmosphere concentrations of sulphur dioxide; less affected by interferences found in other methods; can be fully automated to improve analytical precision; collected samples are analyzed by means of a quick instrumental method

since no sample preparation is required; and humidity does not affect the collection efficiency. A disadvantage of this procedure is that the use of bubbler collection techniques may impose inconveniences including the possibility of spillage during sampling, handling and transportation.

Sampling is conducted by drawing air through a midget-fritted glass bubbler containing a solution of hydrogen peroxide using a personal sampling pump calibrated to within 5% of the recommended flow rate. The suggested flow rate is 1 L/min and the recommended volume collected is between 15 and 60 L. This method was validated over the concentration range of (6 to 26 mg/m^3) 2.5 to 10 ppm for an air volume of 60 L. The qualitative detection limit of the overall procedure is 0.013 µg (0.0041 ppm) for a 12-L air sample. The quantitative detection limit is 0.033 µg (0.010 ppm) for a 12 L air sample.

6.1.6 OSHA Method ID-200

The second OSHA methodology used to determine sulphur dioxide in air (OSHA Method ID-200) consists of using a personal sampling pump to draw a known volume of air through a glass tube containing impregnated activated beaded carbon (OSHA, 1992). The sample is desorbed in a solution of sodium hydroxide and hydrogen peroxide. An aliquot of this solution is analyzed as sulphate by ion chromatography using a conductivity detector. Gravimetric conversion is then used to calculate the amount of sulphur dioxide collected. Advantages of this method include: adequate sensitivity for determining workplace exposures to sulphur dioxide; simple, rapid, and easily automated; and contaminant levels of the sorbent are very low. A disadvantage of this procedure is the need for a desorption efficiency correction which is mass-dependent and may be lot dependent.

Sampling is conducted by drawing air through a glass tube containing impregnated activated beaded carbon using a personal sampling pump calibrated to within 5% of the recommended flow rate. If necessary, a pre-filter cassette assembly can be used to collect particulate interferences. The suggested flow rate is 0.1 L/min and the recommended volume collected is between 1.5 and 12 L. This method was validated over the concentration range of 1.36 to 4.16 ppm using an air volume of 12 L and a flow rate of 0.1 L/min. The qualitative detection limit of the overall procedure is 0.187 µg (0.004 ppm) for a 12-L air sample. The quantitative detection limit is 0.624 µg (0.013 ppm) for a 12 L air sample.

6.2 Alternative, Emerging Technologies

A number of alternative and emerging methods and technologies for monitoring sulphur dioxide concentrations in air have been described. These methods and technologies include passive samplers (sulphation plates, sulphation candles, badges, diffusion tubes), alternative active samplers (impingers, filter packs, detector tubes) and alternative automated techniques (conductimetric analyzers, automated thermodenuder systems, pulsed-fluorescence analyzers, various remote sensors). Refer to Table 13 for a description of individual method advantages and disadvantages.

6.2.1 Passive Samplers

Passive samplers for atmospheric sulphur dioxide have historically been based on the lead sulphation plate or candle technique (Huey, 1968). In fact, sulphation candles have been used to monitor sulphur dioxide concentrations since the 1930s. It is a technique that is recognized by the American Society for Testing and Materials (ASTM) as *G91-97 Standard Practice for Monitoring Atmospheric SO_2 Using the Sulphation Plate Technique* and *D2010/D2010M Standard Test Methods for Evaluation of Total Sulfation Activity in the Atmosphere by the Lead Dioxide Technique* (ASTM, 1971). It is also the technique that Alberta Environment requires industry is to use for the determination of total sulphation (static monitoring) as outlined in the *Air Monitoring Directive: Monitoring and Reporting Procedures for Industry* (AENV, 1989).

This technique depends upon the reaction of sulphur dioxide with lead dioxide to form lead sulphate (Boulerice and Brabant, 1969). The lead dioxide in paste form is painted in a thin layer on a gauze-wrapped cylinder, a glass plate, or other support, and allowed to dry. After exposure to atmospheric sulphur dioxide for a pre-determined period, the lead dioxide layer is removed and a traditional gravimetric procedure or a more sensitive turbidimetric procedure quantitatively is used to ascertain the sulphate content. The result is reported as a sulphation rate in units such as mg of SO_2/100 cm^2/month. Conversion of such a rate to conventional average concentration in ppm sulphur dioxide is highly dependent upon the conditions of exposure and upon the physical form of the lead dioxide. Although in practice a single conversion factor is often used for convenience, resulting in an average concentration which is within a factor of three of an instrumental measurement average.

These samplers are simple and require no power. However, the sampling period is long (i.e. 30 days), they are not specific to sulphur dioxide, and they do not necessarily indicate concentrations in air, rather deposition which is dependent on meteorology. With a standard deviation of 5 % to 10 % and an indeterminate factor for conversion to concentration, sulphation devises are recommended for rough, non-critical applications only. Despite their limited accuracy, the sulphation devices are sufficiently precise for relative measurements. At such low cost and without the need for attendance, the sulphation devises may be liberally used for one-month average sulphation rates.

Passive techniques using badges and diffusion tubes have been developed and employed to overcome some of the accuracy limitations of the lead sulphation technique described above. These passive techniques take samples of sulphur dioxide from the atmosphere at a rate controlled by the natural diffusion of the gas across a membrane but which does not involve active movement of air through the sampler. These samplers are simple, inexpensive, and can be employed spatially at remote locations.

Air monitoring badges are designed to be used either as a personal or area monitor (Krochmal and Kalina, 1997; Kring *et al.*, 1983). They normally consist of a moulded diffuser, a specific sulphur dioxide absorbing solution, and colorimetric reagents in a self-contained package. It begins to sample the atmosphere as soon as the badge is exposed. The intensity of the colour formed by the reagent is proportional to the amount of sulphur dioxide absorbed, which is proportional to the concentration in mg/m^3 (ppm) per hour. Badges are usually made from filters impregnated with various chemicals such as triethanolamine (TEA), $KHCO_3$-glycerine-water, $KHCO_3$, KOH-glycerol, and K_2CO_3.

There are currently no national or international standards governing the application of sulphur dioxide diffusion tubes to ambient air monitoring. However, a number of different types of sample collection and analysis methods have been discussed in the scientific literature (WHO, 1999). The most widely used include using a diffusion tube with triethanolamine (TEA) as an absorbent, glycol as a desorbent, and spectrophotometry as the analytical method; potassium hydroxide/glycerol/spectrophotometry; and sodium carbonate/glycerine/ion-exchange chromatography. In practice, the ion chromatographic technique has been informally accepted as the standard method for sulphur dioxide diffusion tube analysis.

6.2.2 Alternative Active Samplers

The principle of active sampling methodologies is to draw ambient air through a collecting medium (typically a liquid bubbler impinger, filter pack, or detector tube) for a specified time (WHO, 1999; Makkonen and Juntto, 1997; Kok *et al.*, 1990; Anlauf *et al.*, 1986). The volume of air sampled is metered. The collecting medium is subsequently analyzed and the concentration of pollutant in the sampled air is determined. This proven method is well established and has been used in many monitoring networks worldwide for a number of years. Consequently, there is a long history of active sampler sulphur dioxide measurements available. There are several methods of sulphur dioxide monitoring based on this principle. They differ with respect to the solutions used in the collecting medium for sulphur dioxide absorption and the method of analysis. Some of the methods include acidimetry, ion-exchange chromatography, and the Thorin method.

The acidimetric (total acid) method is used to determine a gaseous acid air pollution index (ISO, 1983). Although this method measures total acidity and is not specific to sulphur dioxide, it is adequate for general use. The simplicity of the method and the fact that the reagents are relatively safe makes it a popular choice for routine monitoring. Ion-exchange chromatography is a variation of the above technique. The exposed peroxide solutions are analyzed for sulphate ions by means of ion chromatography, rather than titration. This has the advantage of being sulphate-specific but requires the use of an expensive ion chromatograph. The Thorin method uses hazardous reagents (i.e. perchloric acid, barium perchlorate, dioxane and thorin) that must be handled and disposed of with care (ISO, 1980). Accordingly, this method is not commonly used.

6.2.3 Alternative Automated Techniques

In general, many commercial instruments are available to monitor ambient sulphur dioxide levels in an automated mode. The UV fluorescence and FPD approaches previously described have been extensively evaluated, give detection limits of 2 to 5 µg/m3 (1 to 2 ppb), and are more than adequate for regulatory monitoring purposes. However, a number of alternative and emerging automated monitors have been described which provide many additional benefits. These monitors include conductimetric analyzers, automated thermodenuder systems, pulsed-fluorescence analyzers, and various remote sensors.

The principle of conductivity has had wide application as an analytical procedure for measuring sulphur dioxide in the ambient air (WHO, 1999). Sulphur dioxide has been measured by this

procedure in continuous recording instruments for more than 50 years. This method involves absorption of sulphur dioxide in deionized water containing hydrogen peroxide to produce an acid having conductance sufficient to be detected by a conductivity cell. Conductimetric analyzers generally have good sensitivity, good response, minimal maintenance, and simple operation. The major disadvantage is the susceptibility to interference from non-sulphur gases. Any species that can form or remove ions can interfere to some degree. Instruments employing this principle have been extensively used in the past, however, in recent years they have been replaced with the other methods previously mentioned.

An automatic thermodenuder system for the measurement of sulphur dioxide has been described (Slanina *et al.*, 1987). Air is sampled by Cu/CuO coated denuders tubes in series. When the denuders are heated to 800°C, sulphur dioxide is liberated and detected by a standard monitor. For a sampling time of 30 minutes the limit of detection is between 0.1 and 0.015 μg/m3. This method is not routinely employed because of the complicated procedures required.

Pulsed-fluorescence analyzers operate by photoexciting sulphur dioxide with 214-nm radiation from a Zn lamp (Kok *et al.*, 1990). The resulting fluorescence of the sulphur dioxide is measured photometrically. The detection limit of this technique is 0.2 to 0.3 μg/m3 (0.1 ppb) for a 1-minute averaging time.

Remote optical sensor systems, such as the differential optical absorption system (DOAS) and the differential absorption lidar (DIAL), use long-path spectroscopic techniques to measure the real-time concentration of a pollutant integrated along a path up to 10 km in length between a light source and a detector. DOAS (Kim and Kim, 2001; Mathew *et al.*, 2001) uses a broadband light source whereas DIAL (APREL, 1998) does not. Remote optical sensors can be used to measure sulphur dioxide, but the methods are less established than are those of other automated analyzers. The accuracy and precision of the data from these instruments are, therefore, much more difficult to determine.

Table 13 Method Advantages and Disadvantages

Method	Advantages	Disadvantages
US EPA Reference Method	Specific Simple and inexpensive apparatus Suitable for various sampling periods	Requires immediate analysis Long lag and response time Interferences from NO_x and metals Requires reagent solutions Frequent calibrations and maintenance
US EPA Manual Equivalent Methods	Simple and sensitive Good specificity Based on the reference method	Long lag and response time Interferences from NO_x and metals Requires reagent solutions Frequent calibrations
US EPA Automated Equivalent Methods		
Ultraviolet Fluorescence	Easy to operate High accuracy and low detection limits No other gas required except calibration standards	PAHs may fluoresce at similar wavelengths Some interferences from water and oxygen Expensive
Flame Photometry (FPD)	Extremely sensitive and specific for sulphur compounds Rapid response Low maintenance	Interferences from other sulphur species Hydrocarbons may quench sulphur chemiluminescence May have flame out problem and non-linear response Needs flame gas (hydrogen)
Gas Chromatography with Flame Photometric Detector	Less interferences than FPD	Requires expertise to operate Needs carrier and flame gas Lack of contiguous results
Colourimetry	Simple and sensitive Good specificity Inexpensive	Long lag and response time Interferences from NO_x and metals Requires reagent solutions Frequent calibrations
Infrared Absorption	Very sensitive	More expensive than other analyzers Not yet widely accepted
Coulometry	Stable, simple and specific Low maintenance requirements Less expensive than other analyzers	Requires reagent replacement Requires filters Interferences from may other gases Sensitive to other sulphur species
NIOSH Method 6004	NA	NA
OSHA Method ID-104	Adequate sensitivity Less impact from interferences Simple, rapid and easily automated Humidity does not affect efficiency	Wet chemistry Inconveniences from spillage
OSHA Method ID-200	Adequate sensitivity Less impact from interferences Simple, rapid and easily automated Low contaminant levels	Requires a desorption efficiency correction
Passive Samplers	No moving parts to break down Regular flow calibration unnecessary No bulky, expensive pumps required As reliable as conventional methods	Only reliable at higher ambient concentrations High detection limits Susceptible to meteorology
Alternative Active Samplers	Well established and proven Precise	Labour intensive Expensive Hazardous reagents
Alternative Automated Techniques	Unattended operation possible Better spatial representativeness Minimal maintenance Low detection limits	Expensive Some interferences Accuracy unknown Many not commonly used

*NA denotes not available.

Table 14 List of US EPA Designated Automated Equivalent Methods (US EPA, 2002)

Manufacturer	Model	Designation Number
Advanced Pollution Instrumentation	100	EQSA-0990-077
Advanced Pollution Instrumentation	100A and 100AS	EQSA-0495-100
Teledyne Analytical Instruments	6400A	EQSA-0495-100
ASARCO	500	EQSA-0877-024
Beckman Instruments	953	EQSA-0678-029
Bendix	8303	EQSA-1078-030
Columbia Scientific Industries	5700	EQSA-0494-095
Dasibi Environmental Corporation	4108	EQSA-1086-061
DKK-TOA Corporation	GFS-32	EQSA-0701-115
DKK-TOA Corporation	GFS-112E	EQSA-0100-133
Environment S.A.	AF21M	EQSA-0292-084
Environment S.A.	SANOA	EQSA-0400-138
Horiba	APSA-360, APSA-360-CE, and APSA-360A-CE	EQSA-0197-114
Lear Siegler	AM2020	EQSA-1280-049
Lear Siegler	SM1000	EQSA-1275-005
Lear Siegler, Monitor Labs, or Wedding	ML9850, ML9850B, or 1040	EQSA-0193-092
Meloy	SA185-2A	EQSA-1275-006
Meloy	SA285E	EQSA-1078-032
Meloy	SA700	EQSA-0580-046
Monitor Labs	8450	EQSA-0876-013
Monitor Labs or Lear Siegler	8850	EQSA-0779-039
Monitor Labs or Lear Siegler	8850S	EQSA-0390-075
Opsis	AR 500 and System 300 (open path)	EQSA-0495-101
Philips Electronic Instruments	PW9700	EQSA-0876-011
Philips Electronic Instruments	PW9755	EQSA-0676-010
Thermo Electron	43	EQSA-0276-009
Thermo Electron or Thermo Environmental Instruments	43A, 43B, 43C	EQSA-0486-060

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